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A TREATISE

ON THE

ASSAYING

OF

LEAD, COPPER, SILVER, GOLD, & MERCURY.

FROM THE GERMAN OF

TH. BODEMANN AND BRUNO KERL.

TRANSLATED BY

W. A. GOODYEAR, Ph. B.,

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Illustrated with Plates.

C. T. I.

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PREFACE.

THE work which is here presented was undertaken at the request of members of the Berzelius Trust Association, and two causes have combined to induce its publication. The first of these is the want which has been felt of an accessible guide for metallurgical students in the laboratory of the Sheffield Scientific School; and the second is the extreme paucity, and the general inadequacy of English works upon assaying, while the literature of German science is rich in this direction.

The following pages have been translated from the second edition of TH. BODEMANN'S "*Anleitung zur Berg- und Hüttenmännischen Probierkunst*," enlarged and revised by BRUNO KERL, Clausthal, 1856. This excellent work, which is universally considered as among the best, if not *the* best of the German treatises upon assaying, deserves to be more widely known and more generally used than it has heretofore been in this country.

Our large and rapidly increasing mining interests justify and demand the preparation of a full, reliable, and practical treatise, adapted to the wants of the country, upon the assays of the different metals. Such a work, however, has not yet appeared, and therefore I venture to hope that a translation of the more important part of this valuable German work will not be a useless addition to the literature of American Metallurgy.

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Want of time and other pressing circumstances have prevented me from translating the whole of the work, and I have therefore chosen from among the metals those which seem to be of the most general importance in this country. *Iron*, though fully treated in the original work, has been omitted here, partly for want of time, and partly because convenient methods for its determination are given in accessible works on chemical analysis. *Zinc* has been omitted for similar reasons.

The German assay weights have been retained, instead of reducing them to the French system, as such a reduction would everywhere involve fractions of grammes, unless the quantities of ore, etc., taken, or the proportions of ore and fluxes prescribed for the assays, or both, were changed; and though the changes involved might have been small in quantity, they would still have made the book something more than a translation, which is all it purports to be. The full statement, in the Introduction, of the systems of assay weights employed, with their equivalents in grammes, where custom has given them an absolute value, will remove all difficulty on this account.

The figures (also taken from the German work) represent vessels and appliances which experience has shown to be convenient, adapted to their purpose, and easily obtainable in Europe. In this country it may often be more convenient to use vessels differing somewhat in form, etc., from those here represented. This difference is immaterial *so long as they are adapted to the end in view*, and circumstances will determine how far it may be allowed.

The reader is presupposed to have some knowledge of elementary chemistry, as also some acquaintance with the fluxes, furnaces, fuel, etc., generally used in assaying. The

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latter information can be obtained from MITCHELL'S "*Practical Assaying.*"

Black flux, however, with its concomitants, white flux and raw flux, have been described, though the last two are seldom used. For fuller information also respecting the fluxes, etc.; for the methods of assaying iron, platinum, antimony, bismuth, zinc, tin, nickel, cobalt, chromium, manganese, arsenic, and sulphur; and for copious references to the works of European metallurgists, the reader must be referred to the original work.

Before closing I would acknowledge the obligations which I am under to Prof. GEO. J. BRUSH, of the Sheffield Scientific School, for assistance kindly rendered in the explanation of such technical metallurgical terms and phrases of the German as occur in the work, and with which I was not familiar.

W. A. GOODYEAR.

NEW HAVEN, *May* 1*st*, 1865

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INTRODUCTION.

Assay weights.

THE weights used in assaying in Germany have generally the same subdivisions as the civil weights of the country, but are always made to a much smaller scale.

In Hanover, as well as in a large part of Germany, the centner of the civil weight is divided into 100 pounds, one pound into two marks or thirty-two loth, one loth into four quentchen, and one quentchen into four-fourths.

For the assay of ores, the assay weights derived from the above preserve the same subdivisions, and the absolute weight of the assay centner is generally taken equal to one quentchen of the civil weight = 3.654 grammes. The smallest weight which is then determined on the balance is generally one-fourth or one-eighth of a loth, or respectively 0.2857 and 0.1429 milligramme. One kilogramme = 2,138072 Hanoverian civil pounds.

In the kingdom of Saxony, since the first of January, 1843, the new civil weights of that country have been introduced for the assay of ores. According to this system, the centner (= 50 kilogrammes in weight) is divided into 100 pounds, and one pound into 100 equal parts called pound parts. One centner therefore equals 10000. pound parts. The absolute weight of the assay centner is here taken at 3.75 grammes = 0.75 pound parts. The smallest weight then noted in the assay of silver ores is fixed at half a pound part, which is,

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therefore, .1875 miligramme = .0000375 of a pound part of the civil weight.

At Przibram, in Bohemia, an assay centner of 10. grammes serves as the unit of weight. This centner is divided into 100 pounds, each pound into thirty-two loth, each loth into four quentchen, and each quentchen into four denär. Half an assay centner of ore is generally here weighed out for an assay, and the smallest weight stated in the result is half a pound in the lead assay, and single denär in the silver assay.

At many smelting works an assay centner is also in use, which is divided into 110 pounds, each pound into thirty-two loth, and each loth into four quentchen.

For the assaying of coins, auriferous silver, refined silver, etc., the *mark weight* has been introduced in Germany. The absolute weight of the commercial mark employed for gold and silver is not the same in all places; but the mark is everywhere subdivided in the same way, and the assay weight retains this subdivision.

The mark weight is as follows:

For Gold.			For Silver.			
Mark.	Carats.	Grän.	Mark.	Loth.	Denär or Grän.	
1	24	288.	1	16	256	288
	1	12.		1	16	18

The denär is used almost only in Austria.

The grän is also further divided into four-fourths or eight-eighths both with gold and silver.

In some German States, besides the old subdivisions above, the mark has lately been subdivided into decimal parts, *i.e.* into tenths, hundredths, and thousandths. In *Freiberg*, for example, the mark is taken = one gramme = 1000

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milligrammes, and results are weighed to within a milligramme.

The absolute weight of the assay mark is not everywhere the same. The custom most generally adopted, perhaps, is to take $\frac{1}{16}$ of a loth, civil weight, in the assay of silver, and $\frac{1}{32}$ of a loth, civil weight, in the assay of gold, as the weight of the assay mark.

The absolute value of the unit of weight employed in assaying is a matter of indifference in itself, provided it be so taken as to be convenient for the work and suitable for the capacity of the vessels, etc., employed.

For general practice, however, it is far preferable, at least in the United States of America, instead of these varied German systems, to use the French weights, which combine the advantage of great simplicity with that of being already widely employed and universally understood.

Black flux, white flux, and raw flux.

White flux is produced by deflagrating together equal parts of saltpetre and argol; *black flux*, by deflagrating one part of saltpetre with two to three or more parts of argol. Generally one part of saltpetre and two and a half parts of argol are taken. The finely pulverized and intimate mixture for either flux, before it is deflagrated, is called *raw flux.*

After the saltpetre and argol have been finely pulverized and sifted separately, they are intimately rubbed together, and then deflagrated by throwing the mixture little by little into a low-red-hot crucible, which after each addition is lightly covered over. The deflagration may also be conducted, though less advantageously, by filling the crucible about two-thirds full of the raw flux and then touching it with a red-hot coal or iron. It can only be performed in the open air or under a flue with a strong draft, as the tartaric acid evolves

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various empyreumatic volatile matters in considerable quantity during its decomposition.

With *white flux* the saltpetre suffices to burn all the coal produced by the carbonization of the tartaric acid, and the result is therefore almost pure carbonate of potassa, if pure saltpetre and pure argol have been used. If the latter were impure, the resulting neutral carbonate of potassa may contain several, perhaps ten per cent. of carbonate of lime. White flux works like ordinary carbonate of potassa, which is therefore almost always preferred to the far more expensive *flux*.

With the *black flux* the quantity of saltpetre is not sufficient to burn all the coal from the argol, and there remain therefore in the black flux, according as two, two and a half, or three parts of argol were taken, about five, eight, or twelve per cent. of free carbon, which is mixed in the most intimate manner with the resulting neutral carbonate of potassa—more intimately indeed than would be possible by any mechanical means. This coal does not hinder the fusing of the assay when the flux is used, and effects or promotes the reduction of the metallic oxyds.

Fusion and reduction, sometimes also desulphurization, are the purposes for which black flux is used, and, according to the special character of the assay, a greater or a less proportion of coal to the carbonate of potassa may be desirable, and this is to determine whether two, two and a half, three, or more parts of argol are to be used to one of saltpetre. As a general rule it may be stated, the more difficultly fusible is the assay, the more potassa; and the more metallic oxyd is to be reduced, the more coal; and the more also of the latter, the more oxygen the oxyd contains.

In many cases, instead of black flux, a *mixture* of carbonate of potassa and powdered charcoal, in a suitable ratio to each other, suffices, especially if the mixture, before use, is passed

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through a sieve, or otherwise very intimately mingled. Instead of the powdered charcoal, also, a corresponding (about two to four times as large) quantity of *flour* may be mixed with the carbonate of potassa.

A mixture of one hundred parts of pure carbonate of potassa and ten to fifteen parts of wheat or rye flour is to be preferred to black flux in case the argol contains gypsum, or the saltpetre, sulphates, which in many cases might work injuriously upon the assay. If this is the case, then, in the presence of a reducing flux, sulphid of sodium is apt to form, which, for example in the copper assay, occasions the slagging of copper.

As a perfectly general rule for the use of black flux, and of mixtures similar to it, it is to be observed that the crucible should never be more than two-thirds filled, as the assay always intumesces, *i. e.* evolves gaseous matters, when free carbon is present.

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ASSAY OF LEAD.

DEFECTS OF THE DRY LEAD ASSAY.

We are acquainted with no method by which we can completely separate and determine with accuracy all the lead contained in an ore, metallurgical product, refuse, product of the arts, etc., by a docimastic * assay.

The best methods of assaying in the dry way give the amount of lead with some uncertainty, and always too low, so that the figure of the result obtained must be increased by from $\frac{3}{100}$ to $\frac{12}{100}$, in order to approximate as closely as possible to the *real* value. For example: if a successful lead assay, the results of which are confirmed upon repetition, gives 40 or 50 per cent. of lead, then the *true* lead contents of the sample will generally amount to 44 or 55 per cent. or more. The poorer the substance to be assayed is, the more proportionally does this loss of lead appear to increase. Since, however, a sure check upon this inferior yield is wanting in isolated assays, an addition to the result found is never made in assays intended for mining and metallurgical purposes, but the amount of lead (generally only weighed out to the nearest entire per cent.) is given exactly as it was found.

The inaccuracy of the dry lead assay has its causes

1. In the volatility of the lead.

2. In the presence of substances which alloy with the lead. *Gold* and *silver* go almost entirely into the lead: their weight

* Docimastic, derived from the Greek δοκιμάζειν, to see whether something is genuine or pure, to test, to prove.

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is to be determined, and subtracted from that of the lead regulus obtained whenever it amounts to one per cent. or over. *Copper* is reduced in part, and contaminates the lead the more, the less sulphur there is present. The presence of sulphur tends to retain it in the slag. With one to five per cent. of copper in galena, the copper goes almost entirely into the slag. The amount of copper in the lead button can be determined by the method for the refining of copper, only with very great inaccuracy. *Zinc* remains in the lead in part, especially with poor, very zinciferous ores. *Arsenic* combines with the lead, and by forming a sulphur salt (PbS, Cu_2 S.) As. S_3, occasions a slagging of the lead, and although iron has a stronger affinity for arsenic than lead has, still this sulphur salt is not completely decomposed by iron. Arsenical ores are advantageously roasted beforehand, or in the absence of sulphur moderately heated in a covered crucible in the muffle, which drives off the arsenic in fumes. *Antimony* goes partly into the lead button; but partly into the slag, if the simultaneous presence of sulphur favors the formation of a sulphur salt. The easy fusibility of the compounds of antimony renders in general a partial removal of the antimony by roasting a difficult matter so that, in the difficult separation of antimony from lead, the wet way alone yields accurate results. Although in this case the carbonate of potassa assay of the *Hartz* is better than the *Freiberg* assay with black flux and iron, still the former leaves much to be desired.

3. In the presence of substances which by the formation of sulphur salts dispose the lead to slag, as antimony and arsenic.

If the substances designated under 2 and 3 occur at the same time in the lead ore, the dry way can then be no longer used; *e.g.* with bournonite, with mixtures of galena and fahlerz.

In spite of this inaccuracy, however, the better methods

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are in by far the majority of cases sufficient to determine the value of an ore, or to control the metallurgical work, since the results of the assays remain nearly uniform though only approximate.

With the partial help of the *wet way*, a somewhat more correct result can sometimes be obtained, or an assay of lead becomes possible when the pure dry way ceases to be even approximately trustworthy. A docimastic assay entirely in the wet way, such as we have for copper, has not yet been discovered for lead. The volumetric method also gives only with pure substances, results which are in some degree satisfactory. In this assay, the metal obtained is not directly weighed, but its amount is calculated from the result of a decomposition, and a quantity of incompatible ingredients may therefore be present, which will render the result incorrect, without giving any indications of it.

Classification of Lead Assays.

The choice of an assay method for a plumbiferous substance, is governed mostly by the quality and quantity of the foreign bodies occurring with it. It is the rule in this, to conform the assay as much as possible to the existing local smelting process. The assay methods in general, may be subdivided as follows:—

I.—ORES AND METALLURGICAL PRODUCTS, &c., WHICH CONTAIN THE LEAD COMBINED WITH SULPHUR (OR SELENIUM).

E.g. galena, PbS. with 86.57 Pb. lead matte, selenid of lead, furnace deposits, &c.

A. Ores, &c., containing a *small* amount of foreign *sulphids*, but on the other hand a greater or less quantity of earthy substances, *e. g.* earthy galena or galena slicks.

1. Fusion with carbonate of potassa (*Oberharz*).
2. Fusion with black flux, or carbonate of potassa and flour

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(*Victor-Frederick* smelting works in the Harz, *Holzappel*, &c.)

3. Fusion with black flux (carbonate of potassa and flour, or carbonate of potassa and coal dust*), and iron (*Freiberg*, *Przibram*, *Tarnowitz*; methods at *English* and *French* smelting works).

4. Fusion, with reducing and fusing agents in wrought iron crucibles (methods at *English* and *Belgian* smelting works, at *Stolberg* near Aachen, at *Ramsbeck*, &c.).

B. Ores, &c., containing a *considerable* amount of foreign *metallic sulphids* (zinc blende, iron pyrites, copper pyrites, &c.) or *antimonids* and *arsenids*, with more or less earthy substances.

1. Roasting and subsequent fusion with reducing agents and fluxes (method at the *Communion-Unterharze*).

2. Decomposition with sulphuric acid, and fusion of the sulphate of lead formed with reducing and desulphurizing agents.

C. Poor plumbiferous substances containing a *considerable* amount of *earthy* matters, *e. g.* the waste of preparatory processes, tailings, etc.

1. Smelting with desulphurizing agents and fluxes, and with a weighed quantity of silver.

2. *Rivot's* method of fusion with powerful solvent agents and iron.

3. Indirect method by calculation.

II.—OXYDIZED ORES AND PRODUCTS.

A. The oxyd of lead is combined with fixed mineral acids (sulphuric acid, chromic acid, phosphoric acid, arsenic acid, etc.) *e. g.* in anglesite, pyromorphite, wulfenite, etc.

1. Fusion with reducing agents (black flux, or carbonate

* Throughout this work the term "coal dust" is used synonymously with *powdered charcoal.*

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of potassa and flour, or carbonate of potassa and coal dust), *e. g.* phosphate, molybdate and chlorid of lead, etc.

2. Fusion with reducing agents and iron, *e. g.* sulphate, arsenate and arsenite of lead, etc.

B. The oxyd of lead is free, or combined with silicic acid, carbonic acid, or an organic acid.

1. Fusion with reducing agents (black flux or carbonate of potassa and flour, or carbonate of potassa and coal dust, etc.) *e. g.* litharge, lead skimmings, cerusite, etc.

2. Fusion with reducing and solvent agents (borax, glass, etc.) *e. g.* furnace hearths, lead slag, etc.

III.—ALLOYS OF LEAD.

Assay with sulphuric acid.

SECTION I.

MANAGEMENT OF THE ASSAY FOR ORES AND METALLURGICAL PRODUCTS WHICH CONTAIN THE LEAD COMBINED WITH SULPHUR (*or selenium*).

A. *Ores and metallurgical products which contain a small amount of foreign sulphids, with a greater or less quantity of earthy ingredients.*

1. *Fusion with carbonate of potassa.* At the *Oberharz* smelting house, one centner of the very finely rubbed and pulverized assay substance is weighed out, mixed with three to four times its weight of pure, dry, and finely pulverized carbonate of potassa, and covered over, in a small clay crucible (Fig. 15,*a*) with a layer of decrepitated chlorid of sodium about one-fourth of an inch thick. The assays thus prepared are placed in the thoroughly heated muffle of a large assay furnace (Figs. 1, 2) having a strong draft. They remain in the highest temperature of the furnace, with the mouth of the

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muffle closed with glowing coals, till they have come into perfect fusion (about twenty to thirty minutes). The draft opening is then closed, and at the same time the muffle opened, until the temperature has fallen so far that the crucibles appear brownish-red, and the lead vapors above them have greatly diminished, or have disappeared. At this heat the crucibles, whose contents must, however, always remain in perfect fusion, are maintained, according to the fusibility and composition of the assay sample, and the draft of the furnace, for a longer or shorter time (ten to twenty-five, generally ten minutes). This period, during which the heat is allowed to remain low, is called the *cooling* of the assay.

The furnace is now again brought back to its first temperature, by completely opening the draft and closing the muffle. Ten to fifteen minutes of this last heating are in most cases sufficient. Only poor ores, etc., which contain also a pretty large quantity of arsenic, or of the sulphids of iron, zinc, and copper, are allowed to continue hot five to ten minutes longer.

If one has many assays to make, it will be found advantageous to mix those which contain larger quantities of foreign sulphids, or, by reason of their earthy contents, are difficultly fusible, with more or less *borax*, or, instead of this, to place them in the back and hotter part of the muffle, while those that are very rich in lead and easily fusible, are placed in front, since the latter will be hot enough here, and more easily reached by the air than those deeper in the muffle.

The crucibles, when cold, are broken, the lead buttons obtained are freed from all adhering slag or substance of the crucible, and if the assay were otherwise successful, their weight determined. The assays should not be too rapidly cooled, because the slag is thus easily cracked, and the still half-fluid button lying below is apt to be broken into several pieces.

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In a successful assay, the lead is melted together to a button, deports itself under the hammer and knife like pure lead, and possesses also its color. If the slag shows, upon its surface of separation from the metallic button, lead gray spots with metallic lustre, it will generally also be found that a thin layer of not completely decomposed glistening sulphid or subsulphid of lead has at the same time deposited itself upon the button. This layer, if the above appearance presents itself in a high degree, can be rubbed off or removed in fine scales. The lead button itself then shows upon its surface a high metallic lustre, which does not have the color of pure lead, but a darker and blackish hue. Assays of this kind are to be rejected; they have not been allowed to remain "cool" long enough, or they have in the process become *too* cold; they give the amount of lead too low, and often very considerably so. In assays, which have stood too long in the furnace in the last fusing heat, a very bright button of lead is also found; but here the layer of undecomposed sulphid of lead is wanting, as also the glistening spots on the surface of the slag surrounding the button. If the influence of the heat and air continues too long, then besides a loss through volatilization of the lead, a slagging of the oxyd of lead may take place. A button that is brittle, laminated, and brilliantly white in the fracture, indicates an insufficiency of flux, or the presence of antimony and arsenic. In successful assays the lead button generally has a bluish appearance, which, although not dull, is at the same time not strongly brilliant. The slag must be completely homogeneous, and must have settled down uniformly towards the bottom of the crucible, so that it does not stick in a thick layer to the upper part of the sides of the crucible. It shows by this that it has been in proper fusion. It must have covered over the button in a thick layer (about one-fourth of an inch thick). The chlorid of sodium covering, or a more or less

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colorless slag that is formed, containing chlorid of sodium and carbonate of potassa, overlies in a still thicker layer the true dark-colored slag containing the foreign metallic oxides. A porous slag containing metallic globules indicates a small quantity of flux or too low a temperature; a brilliant vitreous slag, too high a temperature and a slagging of lead. An assay and its duplicate must, moreover, give equal results.

Lead matte and *lead fume* are smelted, with the addition of borax and coal-dust, with carbonate of potassa, and with the first the heat is allowed to last somewhat longer (perhaps to three-quarters of an hour) than with ores. The carbonate of potassa assay gives for lead matte, with its not inconsiderable lead contents (thirty per cent. and over) pretty satisfactory results. Generally the matte is roasted and assayed according to the method described on page 36.

The theory of this lead assay may appear from the following.

If perfectly pure, galena is intimately mixed with three or four times its weight of good dry carbonate of potassa, placed in a clay retort, and this so arranged in the muffle of the assay furnace that its neck projects from the mouth of the muffle, while in the opening of the neck a glass tube is closely fitted, which goes into a receiver, from which it is further prolonged in a second tube, it will be observed that at first only a little water collects in the receiver, proceeding from the small quantity of moisture always present in the carbonate of potassa. Later, with an incipient red heat in the retort, a gas is disengaged, which upon closer investigation proves to be pure carbonic acid gas, *i. e.* free from sulphurous acid (means of proof:—absence of odor; conducting of the gas through a solution of manganate of potassa, reddened by sulphuric acid; through lime and baryta water, and through a solution of caustic potassa, and further examination of the solution of salts obtained). The disengagement

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of gas becomes more active with a stronger red heat, without yielding gases of different composition, but ceases again after awhile. In order to obtain assurance of a complete decomposition, the retort may be kept for an hour at a very strong red heat. After the cooling and breaking of the retort some pure oxyd and carbonate of lead is found deposited in the neck of it, then a pure lead button upon the bottom, and over this a brown slag, free from little globules of lead. It consists in by far the greatest part of sulphid of potassium and still undecomposed carbonate of potassa, but also in small part of silicate of potassa derived from the silica of the retort. If this slag is treated with water till nothing further will dissolve, the substances named can be easily shown to exist in the solution. The solution is colorless, and when supersaturated with acids disengages sulphuretted hydrogen, but throws down no sulphur. In the treatment of the slag with water, sulphid of lead remains behind in black flocks, even the exterior character of which shows that it is not undecomposed galena, but sulphid of lead separated from a chemical combination.

If the brown slag from the retort is placed in a small uncovered crucible and brought back into the hot muffle of the assay furnace and melted, then after some time, whether the slag was covered with chlorid of sodium or not, a button of lead again separates at the bottom of the crucible, and the brown slag now shows itself decolorized. If the crucible is removed from the furnace too soon, only the upper layer of slag is decolorized, and that lying below is still completely unchanged. The decolorized slag consists of carbonate and sulphate of potassa, and no longer contains any trace of sulphid of potassium.

In the above described lead assay, the process now in the strong initial heat proceeds as in the retort, *i. e.* the potassa of the carbonate of potassa is reduced to potassium, while it

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yields its oxygen to the sulphur of the galena and with it forms sulphuric acid; the liberated potassium takes up sulphur from another portion of galena, forming sulphid of potassium. The galena would now in this double way soon lose all its sulphur, if a combination—a sulphur salt—of sulphid of potassium with sulphid of lead did not form, which resists all further action of the carbonate of potassa [$4\ (KO, CO_2) + 7\ PbS = 4\ Pb + 3\ (KS, PbS) + KO, SO_3 + 4\ CO_2$]. The carbonic acid of the thus decomposed carbonate of potassa escapes together with that set free by the sulphuric acid formed, and causes a puffing up of the mass, by which globules of lead already separated are raised up with it, and may perhaps remain with some of the slag sticking to the upper crucible walls. They would here oxydize and produce yellow spots. The covering of chlorid of sodium is designed to guard against loss of lead in this and similar ways. It serves in a certain manner to rinse down the sides of the crucible.

The atmospheric oxygen, in the open crucible, is not entirely excluded by the covering of chlorid of sodium. In the "cooling" of the assay, it oxydizes the sulphur salt contained in the upper part of the slag, forming sulphate of potassa and a portion of sulphate of lead. The latter, during the last high heat, decomposes the sulphid of lead still remaining in the slag, in such a way as to produce metallic lead. ($PbS + PbO, SO_3 = 2\ Pb + 2\ SO_2$.) The reduced particles of lead separate well from the slag thus rendered thinly fluid. Mattes must be allowed to "cool" longer than ores.

The carbonate of potassa assay presupposes in general great practice, and close attention on the part of the assayer; and moreover, if one wishes to find the correct value at once, without fruitless preliminary examinations, and without the necessity of repeating the assay, a general knowledge of the constituents of the assay sample, so far, for example, as this can be obtained by the aid of mineralogy, is necessary. The

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assay after this method, which requires but little preparation, can only be conducted in the muffle furnace, but then in pretty large number (as many as fifty at once). For its success it is indispensably necessary that the "cooling" of the assay be undertaken and stopped again at the right time and in the proper degree. If it is allowed to "cool" too long, too much sulphate of lead is formed in proportion to the sulphid of lead still present in the slag, and in the last heating up, by the action of the two upon each other, easily scorifiable oxyd of lead is produced. ($PbS + 3\ PbO, SO_3 = 4\ PbO + 4\ SO_2$.) If the "cooling" is too soon interrupted, only a small part of the sulphid of lead in the sulphur salt is oxydized, and by the action of the oxydized portion upon the sulphid of lead, sub-sulphid of lead is produced, which either remains in the slag or settles upon the lead button. ($2\ PbS + PbO, SO_3 = Pb_2\ S + Pb + 2\ SO_2$.) Experience gives the only means at hand to guide us here, but leaves us easily in the lurch, so that the result of the assay becomes more doubtful than in some of the methods hereafter described.

With substances containing *antimony* this assay deserves the preference over the others, since most of the antimony remains in the slag in the state of sulphid and oxyd. An addition of saltpetre works advantageously. *Arsenic* and *sulphid of arsenic* mostly go off in fumes during the smelting, but nevertheless always cause the forming of a brittle metallic button. *Sulphid of copper* remains in great part in the slag, but a part of the copper is desulphurized and goes into the lead. If the quantity of copper present is very considerable, the button of metal may be considered as black copper, and refined, and the loss thereby occurring, reckoned as lead.

Proto-sulphid of iron, which occurs, for example, in lead matte, is decomposed by carbonate of potassa, forming metallic iron, which desulphurizes the galena. *Iron pyrites*, on the other hand, occasions the forming of a large quantity of

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sulphid of potassium, and in consequence of this, of a sulphur salt.

It follows, therefore, from the above, that ores, which contain much foreign sulphids, are not suited to this method of assaying, since they cause the production of a large amount of sulphid of potassium, which always retains sulphid of lead. By an addition of saltpetre to the carbonate of potassa, these sulphids may, indeed, be partially decomposed; only an oxydation of the lead is apt to be produced, as well as a mechanical loss by the violent working of the saltpetre.

Bredberg has, in his comparative investigations of the different methods of assaying lead, pronounced the smelting of the raw ore with carbonate of potassa and chlorid of sodium, to be the most inapplicable of all. He cannot, however, have understood the theory of this method, since he melted his assays in the crucible furnace, and, therefore, *without* access of air, and that in his investigations he must, therefore, have found the quantity of lead much too small, is perfectly evident from the above. Thus his opinion in relation to this method must have proved erroneous, and this may be mentioned here for the reason that many a verdict against this method of assaying, has originated in the same, or a similar mistake.

From pure galena, by the carbonate of potassa assay, eighty per cent. of lead at most can be obtained. Calcined *carbonate of soda* is inferior to carbonate of potassa as a desulphurizing agent, and always yields a few per cent. less lead than the latter. According to *Phillips*, seventy-five to seventy-seven per cent. of lead are obtained from galena with carbonate of soda. With *cyanid of potassium* under certain circumstances, the same result can be obtained as with carbonate of potassa, and it does not require so high nor so long continued a temperature; still it offers no real advantage over carbonate of potassa. An addition of thirty to thirty-five per cent. of

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saltpetre to an assay, with which ten parts of carbonate of soda are used, promotes, indeed, the desulphurizing of the lead, but also increases the loss of lead.

At the *Oberharz* smelting house, the lead button is weighed out to pounds, and a difference of five pounds is allowed between different assayers. It is also a custom, though not a correct one, to allow as many pounds' difference as there are tens of pounds in the weight of the lead button obtained. Thus, with a lead contents of thirty and seventy pounds, the difference in the separate assays might amount to three and seven pounds respectively.

2. *Fusion with black flux.*

A modification of the preceding method of assaying, which is sometimes employed, consists in using, instead of the carbonate of potassa, an equal quantity of black flux, or indeed of argol, or in mixing a few per cent. of powdered charcoal or flour with the carbonate of potassa, or in replacing it in part by argol. Too great an addition of carbon diminishes the fusibility of the mass, and hinders the flowing together of the separated particles of lead. By using argol the operation lasts longer, because the mass remains pasty until most of the tartaric acid has been decomposed: but a greater product of lead is obtained. The chemical reaction during the operation is thereby modified so that the carbon of the black flux exerts an influence upon the potassa, and partially reduces it to potassium; the potassium, thus set free, works now as before upon the galena. The latter is thus without the influence of the air more completely decomposed than by carbonate of potassa alone, and the smelting is, therefore, conducted in covered crucibles (Fig. 16) in the wind furnace But since here also sulphid of potassium is formed, and this dissolves sulphid of lead, it is more advisable for the completest possible separation of the lead, to perform the smelting

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in open crucibles (Fig. 15 *a* and 16) in the muffle, in order to allow the atmospheric oxygen to work at the same time on the assay. The product of lead from pure galena does not generally exceed seventy-six to seventy-nine per cent.

At the *Victor-Frederick* smelting works in the Harz, one centner = one hundred and fourteen pounds of galena is mixed with three or four times as much black flux, and with pyritiferous ores ten pounds of borax-glass are added. The mixture is covered with chlorid of sodium, heated for about twenty-five minutes in the muffle furnace with a charcoal fire, and then, after the mouth of the muffle has been opened for about five minutes, taken out of the furnace.

3. *Fusion with metallic iron and carbonate of potassa or soda, or black flux.*

Of poor lead ores an assay centner is placed in the bottom of a crucible (Fig. 16), upon this, according to the richness of the ore in lead, ten to thirty pounds of thick iron wire, above this, about three centner of black flux (prepared with two and a half parts of argol and one of saltpetre), or two to two and a half centner of a mixture of carbonate of potassa and wheat or rye flour (in the ratio of 100 KO, CO_2 to fifteen to twenty of flour), and over all a covering of chlorid of sodium, upon which a small piece of charcoal is laid. If the ore contains basic gang or much quartz, borax (up to forty per cent.) is also added: Barytes and fluor spar fuse without it. Ores which contain larger quantities of metallic sulphids or arsenids (iron pyrites, copper pyrites, mispickel, blende, etc.) are at first moderately roasted on a roasting dish (Fig. 13) that has been rubbed with rouge or chalk, or else moderately heated in a covered crucible, then mixed as above, with the addition of some borax and less iron. If much borax (twenty-five to forty per cent.) is required, it is placed, on account of the puffing up, on the top of the black flux, with

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a smaller portion of borax (ten to fifteen per cent.) immediately on the ore. The smelting takes place either in the wind furnace or in the muffle. In the first case the crucible provided with a cover is set up on a piece of fire-brick, coal is placed around and above it, and the fire is kindled *upon the top*. After the fire has gone down (after three-fourths to five-fourths of an hour) the assay is taken out. If a muffle furnace is used, glowing coals are laid before the crucibles, about as high as their middle, and the assays are smelted for about half an hour after the "flaming" has ceased, at a strong red heat. The lead, buttons freed from slag, and as much as possible from iron, are, in order to remove adhering sulphid of iron, thinly flattened out, then rolled together and weighed.

These assays are executed in the preceding manner at *Freiberg*. They are weighed out to within one pound, and the contents stated for every five pounds through all grades of richness.*

At *Przibram*, with ores containing galena, one-half an assay centner (five grammes) is mixed with one hundred and fifteen to one hundred and twenty pounds black flux (two argol and one saltpetre), ten to twelve pounds borax, and eighteen to twenty pounds iron wire. With blendy ores, to one-half centner of ore, two hundred pounds black flux, ten to twelve pounds borax, and twenty to twenty-five pounds iron wire are taken. Two to three per cent. of saltpetre are mixed with the chlorid of sodium that serves as a covering, in order to render it more easily fusible, and to retain the lead that would otherwise volatilize by oxydizing it.

This method of assaying depends upon the fact that galena, in the smelting with metallic iron, yields the whole of its

* *i. e.* quantities less than five pounds are not stated in the results; thus, if the actual result was sixty-seven pounds it is stated as sixty-five, if it was sixty-eight pounds it is stated as seventy, and so on.

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sulphur to the iron, while metallic lead is formed, and a mixture of different sulphids of iron (FeS, and Fe_2 S) is produced, one hundred parts of galena, which contain 13.45 sulphur and 86.55 lead, require for their complete decomposition, upon the supposition that only the protosulphid FeS, which consists of 37.23 sulphur and 62.77 iron, is formed, 22.67 parts metallic iron. The prescribed addition of iron then remains fully sufficient, even when it is also taken into consideration that a part of the iron is claimed by foreign substances contained in the assay sample, namely by pyrites, arsenic, sulphid of antimony, etc.

The lead in this assay, if it is not exposed to an unnecessarily strong heat, does not indeed alloy with the iron: still the iron should not be used in the shape of *filings*, since then the assayer would expose himself to the danger of a mechanical contamination of the lead button by finely divided iron; moreover, because small globules of lead might be retained in the slag thus rendered more difficultly fusible by too large an addition of finely divided iron. By using iron wire, what iron is not consumed by the assay is found still hanging together in a single piece.

The alkaline carbonate of the black flux, although here specially brought into use only to form a slag, facilitates also the decomposition of the galena, since it works upon it in the manner already discussed. The sulphid of potassium hereby produced does not require to be decomposed by the atmospheric oxygen, that it may yield again the sulphid of lead dissolved by it, since this sulphid of lead also is decomposed by the iron. This lead assay can therefore be also conducted in covered crucibles in the crucible furnace, since the gases disengaged at first easily find an outlet through the light luting of the cover.

By using black flux its coal works likewise in the way already stated; but the liberated potassium is apt to conta-

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minate to some extent the lead obtained by the assay. The carbon of the black flux hinders the oxydation of the lead.

The assay is to be considered as successful if duplicates agree, and the lead has flowed together to a *single* button, and small globules of lead do not, as is the case with too low or too short a heat, stick either in the matte surrounding the lead button (sulphid of iron, and other existing and not decomposed sulphids or arsenids contained in the assay sample), or to the iron wire remaining behind, and moreover the slag shows that it has been in sufficiently thin fusion.

This method of assaying yields a few (up to 8) per cent. more lead than the carbonate of potassa assay, because the amount of lead retained in the slag, in the sulphurated or oxydized state, is diminished by the presence of the iron and the carbon. From galena with 86.5 per cent. of lead, 84.85 per cent. are obtained; nevertheless, with impure ores the loss of lead may rise to 10 per cent. or more. The care of the fire, whether one works in the wind furnace or the muffle furnace, is very simple, and a failure of the assay, even by complete ignorance of the constituents of the assay sample, is far more rare than in the carbonate of potassa assay. This assay has moreover the advantage that it can be conducted in either the wind or the muffle furnace, but on account of the greater capacity of the smelting crucible, so many assays cannot be placed in the furnace at a time as in the carbonate of potassa assay.

As drawbacks to this assay we may notice especially, that a lead button containing potassium is apt to be obtained, that little globules of lead are apt to remain sticking to the iron wire, and if the assay sample contains antimony, arsenic, and copper, these metals are mostly reduced by the iron, and brought into the lead button. At *Freiberg* ores containing *antimony* are at once smelted with black flux and coal, without iron, to an antimonial lead button, and an empirical cor-

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rection of 10–15 per cent. is then subtracted. With *zinckiferous* ores, if they are partially roasted beforehand, or are furnished with a large addition of black flux and some borax, this method gives satisfactory results.

The following modifications of this method are found in different countries.

1. One modification, which is not, however, to be recommended, consists in adding oxyd of iron, perhaps forge scales, instead of metallic iron. In this case black flux is always chosen as the flux. Its carbon reduces the oxyd of iron, which then works as above. To this modification, however applies precisely what was said against the use of iron filings (page 32), and it may also occasion errors in another way; since if too small a quantity of forge scales is used, and the access of air prevented, all the sulphid of lead is not decomposed.

2. Galena is smelted with thirty per cent. of iron (small nails, pieces of iron wire, etc.) with a covering of carbonate of soda, chlorid of sodium or borax, at a strong red heat, and by this are obtained, according to *Phillips*, as high as seventy-eight per cent., according to *Berthier* seventy-two to seventy-nine per cent. of lead.

3. The French assayers use, for the decomposing of the galena, carbonate of soda, saltpetre, borax, and iron, which last, in the shape of a horse-shoe of plate iron, is moved about in the melted mass until no more globules of lead attach themselves to it (*Rivot's* method). From pure galena eighty-two to eighty-four per cent. of lead are obtained.

4. *Overmann* recommends the smelting of one part galena with one part saltpetre, two parts argol, some carbonate of soda, and one-fifth of the weight of the ore, in iron filings, with a chlorid of sodium covering, in a copper crucible, by which generally only five per cent., rarely over ten per cent. loss of lead occurs. The chlorine in the chlorid of sodium aids in the slagging of the iron, copper, etc.

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4. *Fusion with reducing agents and fluxes, in wrought iron crucibles.*

Upon the bottom of a wrought iron crucible, perhaps three inches high and 2-2½ inches in wide, which is brought beforehand to a red heat, are placed twelve to twenty-five grammes (4-8 centner) flux (carbonate of potassa or soda, or two saltpetre, three argol, and one borax), and upon this twenty-five to fifty grammes (8-16 assay centner and more) of the assay substance, which is covered over with a layer of powdered glass or common salt, and exposed in covered crucibles, to perhaps a quarter of an hour's strong heat, with charcoal or coke in the wind furnace. When complete fusion has ensued, the contents of the crucible are poured out in a pouring plate, or into a conical mould with the precaution to have the slag remain behind in the crucible as much as possible, which is promoted by holding a chip or splinter of wood before it. The slag is again smelted ten to fifteen minutes with carbonate of potassa; then the mass is poured out and the crucible used again,—sometimes as many as twelve or fifteen times.

This management gives, especially by using larger quantities of the assay substance, good results in the product of lead (as high as eighty-four per cent. from pure galena), and the expense in time, but not many assays can be conducted simultaneously.

B. *Ores and metallurgical products which contain a considerable quantity of foreign sulphids (zinc blende, iron pyrites, copper pyrites, &c.), or arsenids and antimonids (mis-nickel, bournonite, &c.), and a greater or less amount of earths.*

General remarks.

For substances of this kind (for example poor lead matte) the methods of assaying described under A. are not suitable;

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because, on the one hand, the assay is rendered much more difficultly fusible by the sulphids present, and requires a higher and more prolonged temperature, in order that the small quantity of lead separated may flow well together into a button; and on the other hand, the affinity of the sulphid of lead and the sulphid of potassium formed for these sulphids, hinders the decomposition of the first, and this is the more sensibly the case, the more predominantly the latter are present. By an addition of iron, the remnant of sulphid of lead might be decomposed, but this would also partially decompose the other sulphids, and their radicals would go into the lead.

For substances of this character, only the roasting assay, and the assay with sulphuric acid are suitable.

1. *Roasting and reducing assay.*

This method is in use, among other places, at the *Communion-Unterharz* smelting works, where ores are smelted that contain sulphids (copper pyrites, iron pyrites, zinc blende, &c.), antimonids, arsenids, and earths (barytes, quartz, calc spar, clay slate) in such large quantity, that in the large way, the ore already roasted three times, only contains six to eight per cent of lead.

Two assay centner of ore, matte, &c., are heated at first at a low red heat in the muffle, on a roasting dish that has been previously rubbed with chalk. After ten to fifteen minutes, they are taken out of the furnace, then again roasted at a moderate temperature for ten or fifteen minutes with frequent turning of the dish. The assay is then once more taken from the furnace, allowed to cool, rubbed up in an agate mortar and again roasted for half an hour, whereupon it is taken out of the furnace; tallow is added while it yet glows, and it is again brought to a strong red heat. The rubbing up and calcining with tallow, is repeated several times more, and when

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afterwards the assays shall have been exposed for two hours continuously to a strong red heat, with the mouth of the muffle almost entirely closed, if no more sulphurous acid vapors escape, the roasting is considered as finished. This lasts six to twelve hours. The roasted sample is then portioned out with the balance, each portion mixed with three or four parts of black flux and an equal quantity of borax and glass, placed in a small crucible (Fig. 16 or 17) covered with chlorid of sodium, furnished with a little piece of coal and a cover, and smelted in the wind furnace, for about a quarter of an hour after the fire is well ignited. Assays that have worked well give nearly equal malleable buttons that do not contain matte, and a black uniformly fused slag.

The purpose of the roasting is to convert the metallic sulphids, arsenids, and antimonids into oxyds. But since in the process, sulphates, antimonates and arsenates are produced, we seek to destroy these by repeated calcining with tallow (see above), instead of an intermixture of coal-dust or flour. By melting the roasted assay with its charge at *not too high* a temperature, the oxyd of lead is reduced, and the foreign oxyds and earths contained in the sample are, by the aid of the potassa in the black flux, as well as of the borax and glass, slagged off. If sulphates or sulphids should have still remained behind in the roasted ore, they will yet in the smelting be partially desulphurized by the working of the oxyds, especially of the oxyd of iron. An addition of metallic iron would in this connection be advantageous.

The roasting is a time-consuming process, and one which causes not an unimportant loss of lead. If it is not done thoroughly, then, in the reduction smelting, sulphur salts are formed, which always retain lead, as also a plumbiferous matte, which surrounds the lead button. By the use of too high a temperature in the smelting, a great part of the foreign oxyds is reduced, and the lead becomes contaminated. This

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reduction, however, cannot be entirely avoided, even with a rightly conducted temperature.

Galena melts indeed less easily if the air is excluded, than metallic lead; but is much more volatile than the latter, and is decomposed by fusion into a higher sulphid which is volatile and a lower one (Pb_2S) which remains as a residue By roasting, galena gives a mixture of oxyd and sulphate of lead, from which last the sulphuric acid cannot be separated, even at a fusing temperature. Sulphate of lead becomes soft by heat, fuses at a bright white heat, and is converted by carbon, with a considerable loss of lead through volatilization, into oxyd of lead, metallic lead, or subsulphid of lead, according to the quantity of carbon used and the temperature employed. With oxyd of lead, the sulphate easily fuses together.

2. *Assay with sulphuric acid.*

The assay sample is rubbed as fine as possible. A suitable quantity of it—two or more assay centner, is then weighed out for an assay, and boiled with four to eight times its weight of oil of vitriol until all is decomposed. All excess of sulphuric acid is then evaporated in a porcelain capsule, under a flue with a good draft, and the mass carried to dryness. Boiling sulphuric acid decomposes the sulphids, changing iron, copper, nickel, zinc, &c., into salts which dissolve readily in water, and also at the same time changing the sulphid of lead into sulphate, which in water, especially in water that is cold, and also contains free sulphuric acid, is as good as insoluble. The decomposition of the ore is in general accelerated by first heating it with nitric acid or aqua regia, and then, with the addition of sulphuric acid, evaporating to dryness. The dry mass, when cold, is moistened with a small quantity of sulphuric acid, and with cold water, by the aid of a small brush, is brought without loss upon a small filter,

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and washed with cold water until the filtrate is colorless. Unnecessary prolonging of the washing is to be avoided, for sulphate of lead is not absolutely insoluble. The filter, with its contents, is dried in the funnel, until it can be easily taken out of it without tearing. It is now laid immediately into the clay crucible, in which the sulphate of lead is afterwards to be reduced, and this is placed in a very gentle stove warmth. (Some carbonate of potassa may be first poured into the bottom of the crucible.) When completely dry, the crucible, with the cover laid over it, is very gently heated, so that the filter carbonizes, which very soon happens, as the free sulphuric acid is not completely soaked out. The filter is now stirred up with a little rod, black flux, or carbonate of potassa with coal-dust and iron are introduced into the crucible, and intimately mixed with the sulphate of lead and the rest of the insoluble residue. About four or five times the volume of the whole residue are taken of black flux, and the assay is further treated, as prescribed in the portion which follows upon the assaying of sulphate of lead.

In this way the lead is concentrated, and the foreign sulphids, which were specified above as the cause of the failure of the assay in such cases, completely removed. The result obtained in this way is satisfactory and deserves the same confidence as one obtained in favorable circumstances by the ordinary lead assay from an ore with a medium or high percentage of lead.

C. *Poor plumbiferous substances containing a considerable quantity of earthy matters (tailings, slimes, &c.).*

1. *Fusion with fluxes and a weighed quantity of silver.*

The assay is mixed as ordinarily with carbonate of potassa or black flux, and thirty to fifty pounds of accurately weighed, refined silver are added in a finely divided state. In the smelting, the silver assists in the better union and collection

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of the separated globules of lead. From the whole weight found, the weight of the silver added is then subtracted. In the presence of antimony, arsenic, &c., this method gives no reliable result.

2. *Fusion with solvent agents and iron.*

According to *Rivot*, one hundred grammes (about thirty assay centner) of the pulverized substance are mixed with one hundred to one hundred and fifty grammes, of caustic soda, and one hundred and fifty to two hundred and fifty grammes (according to the quantity of earths present) of calcined carbonate of soda, put into a smelting crucible, and an iron plate one inch wide and one and a half lines thick, bent into the form of a horse-shoe, is so stuck into the mixture that both ends rest upon the bottom of the crucible, while the bent part projects free above the mass. The crucible, covered with a few good-sized coals, is placed in a wind furnace, so that it stands only about two inches below the mouth of it, and then with the dome placed over it, slowly heated up. After fifteen to twenty minutes, if the mass has become fluid, the assayer stirs it continually about with the iron, and draws the latter out from time to time in order to observe whether little globules of lead still stick to it. When this is no longer, or only imperceptibly the case, the process is ended; the crucible is removed from the furnace, and either its contents are poured out, or after cooling the crucible is broken.

3. *Indirect method by calculation.*

The lead contents of slimes are calculated in the following way. It is assumed that if the quantities of lead and silver in the slick from which the slimes came are known, the quantity of lead will bear the same ratio in the slime as in the slick, to the quantity of silver, which last can be found with sufficient accuracy. Thus for example, if a galena slick contains sixty pounds of lead and five loth of silver in the centner, and

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the slime coming from it contains $\frac{1}{16}$ loth silver, the amount of lead contained by it, is $\frac{60}{16 \cdot 5} = .75$ pound.

SECTION II.

ORES, METALLURGICAL PRODUCTS, ETC., WHICH CONTAIN THE LEAD AS OXYD.

A. *The oxyd of lead is combined with fixed mineral acids.*

1. *Fusion with reducing agents.*

A centner of the substance to be assayed is intimately mixed with three or four times its weight of a black flux rich in carbon, or with a similarly working mixture of an equal quantity of carbonate of potassa with twenty to thirty pounds of coal dust, or of carbonate of potassa and argol or flour, and smelted in a clay crucible, after the mixture has been previously covered over in the crucible with a thick layer of chlorid of sodium, carbonate of potassa, or black flux.

To this treatment are subjected substances (*e. g.* pyromorphite, wulfenite, crocoisite, &c.) whose acids combine, either directly or after partial reduction, with the alkali, while the freed lead is reduced. Tungstic acid, molybdic acid, and phosphoric acid are not reduced at all by the temperature to be employed; chromic acid on the other hand passes into sesquioxyd of chromium, which remains suspended in the slag.

If the assay sample contains much *earthy ingredients*, an addition of borax or glass may be necessary.

In the smelting it must be seen to that the temperature does not rise too rapidly, for as soon as the mass begins to grow soft, gases are evolved very copiously, and occasion an energetic rising up in the crucible. This is especially the case in all lead assays in which the fluxes contain carbon. This stage is called *the flaming of the assay*, since the car-

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bonic oxyd and carburetted hydrogen gases escaping from the mass, with open crucibles, take fire and burn with flame above them. Only when this foaming up has somewhat abated should the heat be increased.

With respect to the duration of the smelting, the indications of a successful assay, &c., what was said for substances in the first part, holds good here also.

2. *Fusion with reducing agents and iron.*

If the oxyd of lead is combined with sulphuric, arsenious or arsenic acid (*e. g.* in lead vitriol, roasted galena and matte, lead waste and dross, lead smoke, slags with sulphate of lead, &c.), then, in the charging, besides three or four parts of black flux, an addition is made of ten to thirty per cent. of iron, in order to decompose the sulphids and arsenids formed in the reduction smelting. The liberated arsenic and antimony partly pass off in fumes and partly go into the lead button. If sulphate of lead is present, the assay may also, instead of receiving an addition of iron, after fusing, be allowed to "cool" awhile.

B. *The oxyd of lead is free, or combined with silicic, carbonic, or an organic acid.*

1. *Fusion with reducing agents.*

The assay sample, free from difficultly fusible substances, is smelted in a clay crucible, with three to four times its weight of a black flux rich in carbon, or with a similarly working mixture of carbonate of potassa, and flour or coal-dust, under a thick covering of chlorid of sodium, or carbonate of potassa. Whether this smelting takes place in open or covered crucibles is indifferent, since no access of air is necessary, only regard must be had to the "flaming" of the assay.

If sulphur is supposed to be present (*e. g.* in skimmings), an addition of five to ten pounds of iron may be given. A

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period of thirteen to fifteen minutes after the fire is well ignited generally suffices for the smelting in the wind furnace; and in the muffle about half an hour after the "flaming."

Carbonate of lead loses all its carbonic acid by heat alone, and so is *acetic acid* or any other organic acid decomposed by heat alone; *silicic acid* when present combines with the potassa of the flux, so that in this class of substances a simple reduction ensues, brought about by the carbon of the fluxes added.

Litharge, skimmings, &c., are in general completely reduced by a moderate red heat (somewhere in the front of the muffle) in half an hour, and their lead contents melted together to a button. A higher or more prolonged heat would only cause a volatilization of the lead.

The slag must come into thin fusion, and since this depends very much upon the character of the ingredients of the assay sample, the degree and duration of the heat, in the smelting, must be moderated accordingly.

2. *Fusion with reducing and solvent agents.*

Compounds of oxyd of lead which contain difficultly fusible ingredients (*e. g.* lead slag, furnace hearths, &c.) are, in addition to black flux, also mixed with solvent agents (borax, glass) up to an equal weight (generally only with twenty to forty per cent.) and left in the furnace till they are in perfectly thin fusion (with difficultly fusible slags, one and a half to two hours in an ardent red or incipient white heat). To slags containing sulphur an addition of five to ten pounds of iron is given (*Freiberg*), or they are previously roasted (*Unterharz*).

With poor slags, &c., two assay centner are often taken for an assay; and here also the addition of a weighed quantity of pure silver may sometimes be of use for the better collection of the little lead that separates out.

In *Freiberg*, slags in which a quarter to half per cent. of

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lead can be shown, are mixed with black flux, twenty to forty per cent. borax and five to ten pounds iron, with the addition of a weighed quantity of silver. With very rich slags coal dust is also added. At *Przibram*, half centner (five grammes) of slag are mixed with two hundred pounds black flux, twenty-five pounds borax, and seven pounds argol. At the *Oberharz* smelting-house, two centner of slag are mixed with carbonate of potassa, coal dust, and some (twenty-five to thirty pounds) borax, and smelted for one and a half hours after the "flaming," in the muffle. At the *Unterharz* smelting works, two centner of slag are roasted similarly to lead ore (page 36) only without calcining with tallow, for six to eight hours, then separated into parts, and each portion smelted with three or four times its weight of black flux and once its weight of borax and glass, in the wind furnace for a quarter to half an hour after the fire is well ignited. In the muffle the assays are smelted after the "flaming" three quarters of an hour, and then allowed to "cool" for five minutes before being taken out. At the *Unterharz* smelting-house, the Oberharz slags are smelted with black flux, glass and borax, with a covering of chlorid of sodium in the muffle for half an hour after the decrepitation has ceased, then allowed to "cool" five minutes and taken out. In the wind furnace, the assays are allowed to remain thirteen to fifteen minutes after the fire is well ignited.

The smaller is the amount of lead in the substance to be examined, the less reliable in general is the result of the assay. Accurate results can then only be reached by an analytical process, by which, if only the determination of the lead is required, this end can often be attained pretty quickly.

The lead obtained by this reduction smelting is, excepting, perhaps, for an exceedingly small, and therefore to be neglected quantity of potassium, pure, unless easily reducible foreign metallic oxyds, particularly those of copper, antimony, tin and

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bismuth were also contained in the assay. If on the other hand oxyds of this kind are present, the lead will be more or less contaminated by the corresponding metals. The quantity of them contained in the lead separated, must then be determined by a special examination, and deducted from the weight of the alloy, in order to obtain that of the pure lead.

If the lead contains *antimony*, it is treated with pure moderately strong nitric acid until complete decomposition ensues; the excess of acid is then evaporated in a porcelain capsule, the separated oxyd of antimony placed upon a dried and weighed filter, and the oxyd of lead completely washed out with hot distilled or rain water. The filter with its contents is then completely dried at 100° C. and from the weight, after deducting that of the filter, the amount of antimony is calculated. 100 oxyd of antimony = 84.3 antimony. Any copper, tin or bismuth present is to be determined in the manner given in the assay of these metals. If gold or silver is present, the rule given upon page 17–18 is to be observed.

Section III.

ALLOYS OF LEAD.

1. *Assay with sulphuric acid.*

No docimastic assay is known for exhibiting the lead isolated from its alloys. In individual cases a serviceable result may be attained, if the metal (*e.g.* of copper by refining *it*) with which the lead is combined be determined, and its quantity then deducted. This method is however in general, the more unreliable, the smaller is the quantity of lead, or when the lead is alloyed with several metals; so that then the quantity of lead can often only be determined by the partial or complete aid of the wet way.

For many products (*e.g.* crude lead, hard lead—containing antimony or arsenic—plumbiferous copper, &c.) the assay with

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sulphuric acid described on page 38 is suitable. One assay centner of the substance is decomposed by nitric acid or aqua regia, then with the addition of sulphuric acid evaporated to dryness, and the dry mass treated as above directed. If the residue consists only of sulphate of lead, it can be brought upon a weighed filter, and from the weight of the residue after drying, the amount of lead may be calculated. 100 parts sulphate of lead contain 68.33 parts lead.

ADDITIONAL REMARKS ON THE LEAD ASSAY.

Comparison of the different methods for the docimastic determination of lead in their application to various products.

Markus has made the following comparative experiments with the methods of assaying lead ores most in use at the Austrian smelting works at *Joachimsthal.*

a. Assay with black flux and iron.—One assay centner (5.7 grammes) of the finely rubbed, sifted, and dried assay substance was mixed with two assay centner of black flux made of sixteen saltpetre and forty argol, and sixty pounds of borax-glass in a mixing capsule, and put into a clay crucible, on the bottom of which a piece of thick iron wire 1″ long and forty pounds in weight, had been placed in a vertical position. The crucible charge, covered over with two centner of decrepitated chlorid of sodium, was smelted in a mineral coal muffle furnace, with the mouth of the muffle closed, and the draft half open, at a moderate temperature, the temperature then lowered for six to seven minutes by opening the mouth of the muffle, then the muffle closed again for an equal period, and the final heat then given. The cessation of the low crackling of the assay was now carefully attended to, and this, ceasing after seven to eight minutes, indicated the completion of the assay. The duration of the assay, by the way, was twenty minutes.

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b. Roasting and reduction assay with iron.—One assay centner of galena was roasted, at first with a low temperature, for about thirty minutes on a roasting dish, and the dish then pushed into the back part of the muffle for six to eight minutes to destroy the sulphates formed. The roasted ore was rubbed fine, intimately mixed with three hundred pounds of black flux and fifty pounds of borax-glass, placed in a crucible with a piece of iron weighing twenty pounds at the bottom, covered with salt, and smelted as above.

c. Roasting and fusing with black flux.—One centner of the roasted ore was smelted as before with three hundred pounds of black flux and fifty pounds of borax, but without iron.

The results obtained proved:

1. That with all those products which contain tolerably pure sulphid of lead, especially with high percentages, the iron assay, *a*, gives in a remarkably predominant degree the most lead (as high as ninety-six per cent. of all the lead present).

2. With impure lead ores, which contain more foreign sulphids, the assay *a* gives likewise the highest percentage, though the assays *b* and *c* give only a few per cent. less.

3. If foreign sulphids are present in predominant quantity, the methods of *b* and *c* give a slightly higher percentage than that of *a*.

Levol's fusion assay with ferrocyanide and cyanide of potassium.

According to Levol, the method of assaying galena for its lead by smelting it with black flux and iron is defective in two respects. First, it is difficult to choose precisely the quantity of iron required for the reduction of the lead, and a lack or excess of it either gives too little lead or a button containing iron; and second, in order that the reaction may

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be complete and the lead unite to a button, we are compelled to use a very high temperature, at which lead volatilizes. The first defect can indeed be removed by the use of iron crucibles, but these are easily rendered unserviceable, and require a pouring out of the fused mass, and then globules of lead are apt to remain in the slag.

By the use of a mixture of fifty parts of cyanid of potassium and one hundred of anhydrous ferrocyanid of potassium to one hundred of galena, the loss of lead diminishes to from two to two and a half per cent., probably in consequence of the easy fusibility of the mixture and the extremely fine division of the iron in the ferrocyanid of potassium. With antimonial galena this process is not applicable, as the antimony is reduced and goes into the lead. Cyanid of potassium alone gives, by reason of the greater quantity of metallic sulphid which it retains, a smaller product of lead.

Schemnitz lead assay.

To one centner of well roasted powder, two centner of black flux (of one and three-quarter parts saltpetre and two parts argol), six to eight pounds of borax, and a chlorid of sodium covering.

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ASSAY OF COPPER.

CLASSIFICATION OF THE COPPER ASSAY.

For no metal does the art of assaying possess so many different methods of examination, partly more or less similar to each other, and partly based upon very different principles, as for copper. The different substances to be examined for copper, are very often of exceedingly various composition; and thus, particularly from this circumstance, since copper is marked by no specially prominent and distinctive chemical properties; as well as from the commercial value of copper, and from custom and locality, have the different methods of assaying arisen. Certain *methods in the dry way* give for definite, little complicated substances, such for example as a more or less constant and uniform mining and smelting process yields, useful and reliable results, but cease altogether to be even practicable for other, differently composed, or poor cupriferous substances.

In general, the *methods in the wet way* are to be preferred, since they remain practicable in the great majority of cases, and with multifariously changing constitution of the assay sample, still yield sufficiently trustworthy results. But they require in general a closer acquaintance with chemical manipulations and reactions, while the dry assays demand more skill than science.

The alloys of copper used in the arts and in common life, give by the docimastic assay in the wet way, in general cor-

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rect results, that can in most cases be used to good advantage, but are sometimes inferior in accuracy to an analytical examination; so that in general, the amount of copper, in ores and metallurgical products, can be determined with complete accuracy only by analysis.

The copper assay may be classified in the following manner:

A. *Assays in the dry way.*

I. SULPHURETTED ORES OR PRODUCTS WITH OR WITHOUT ACCOMPANYING SELENIUM, ANTIMONY, OR ARSENIC.

A. *Assays for rich ores and products.*

(*Copper glance*, Cu_2S with 79.7 Cu; *Chalcopyrite*, Cu_2S, Fe_2S_3 with 34.4 Cu; *Erubescite*, $3Cu_2S$, F_2S_3 with 55.7 Cu; *Bournonite*, $3Cu_2S$, $SbS_3+2[3PbS, SbS_3]$, with 12.7 Cu; *Fahlerz*, $4[Cu_2S, FeS, ZnS, AgS, HgS]$, $[SbS, AsS_3, Bi_2S_3]$, with 30.–48. Cu; *Covelline*, CuS with 66.7 Cu; *Wolfsbergite*, Cu_2S, SbS_3 with 24.9 Cu; *Domeykite*, Cu_3As with 71.6 Cu; *Copper matte*, *Copper speiss*, etc.

1. *German Copper Assay.* Roasting, smelting to black copper, refining of the black copper on the cupel or on the refining dish.

2. *English Copper Assay.* Fusing the raw ore to a matte, roasting and smelting of the matte to black copper, refining of the black copper, and reduction of the slag thus produced.

3. *Plattner's Copper Assay.* Formation of arsenid of copper, and refining of the same.

B. *Assays for poor ores and products.*

1. Fusion of the ore, etc., to a crude matte, and further treatment of the same according to A. I.

2. Fusion of the roasted ore with agents to collect the cop-

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per (lead, antimony, or arsenic), and refining of the black copper.

II.—OXYDIZED ORES AND PRODUCTS.

(*Red copper*, Cu_2 O with 88.7 Cu; *malachite*, 2 Cu O, CO_2+HO with 57.3 Cu; *azurite*, 2 Cu O, CO_2+Cu O, HO with 55.1 Cu; *cyanosite*, Cu O, SO_3+5 HO with 25.3 Cu; *phosphate of copper* with 30.–56. Cu; *arsenate of copper* with 25.–50. Cu; *chromate*, *vanadate*, and *silicate of copper; slags*, etc.)

1. *Reducing* and *solvent fusion* with or without collecting agents (antimony, arsenic, lead), for the copper, after the ore has been roasted if necessary (*e. g.* with cyanosite and arsenate of copper), with coal dust, graphite or carbonate of ammonia.

2. *Concentration smelting* with pyrites to a matte, which is roasted and smelted to black copper with or without collecting agents for the copper.

III.—COPPER ALLOYS.

Refining with lead on the cupel or with borax on the refining dish, with or without the addition of lead, antimony, or arsenic.

B. *Assays in the wet way.*

I.—ASSAYS FOR SUBSTANCES RICH IN COPPER.

A. *The modified Swedish assay.*—Precipitation of the copper from its solution by iron or zinc.

B. *Colorimetric assays*, including:

1. *Jaquelin's* method.

2. *von Hubert's* method.

3. *Müller's* method with a complementary colorimeter.

C. *Volumetric assays*, including:

1. *Pelouze's* method by precipitation with sulphid of sodium.

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2. *Schwarz's* method by oxydation with permanganate of potassa.

D. *Other assays* after *Levol*, *Byer* and *Robert*, *Rivot*, etc.

II.—ASSAYS FOR SUBSTANCES POOR IN COPPER.

(Slags, lead containing copper, copper slate, etc.)

Heine's colorimetric method.

SECTION I.

A. COPPER ASSAYS IN THE DRY WAY.

I.—SULPHURETTED ORES AND PRODUCTS, WITH OR WITHOUT ACCOMPANYING SELENIUM, ARSENIC, OR ANTIMONY.

A. *Assays for rich ores and products.*

1. *German copper assay.*

This assay comprises the following operations:

1st. The *roasting in the muffle furnace.*

From the correctly chosen, properly dried and prepared assay substance, one centner is weighed out in duplicate for the assay. The weighed substance is so spread out with a spatula from the centre outwards on a roasting dish (Figs. 10–11) that has been previously rubbed with chalk, rouge, or powdered manganese, that most of it lies towards the margin of the dish, and only a thin layer is found in the middle. The assay, which has also been previously well mixed with at least two parts by volume of charcoal powder, or twenty-five to forty pounds of graphite, is then placed in the low red-hot muffle and cautiously roasted till no more sulphurous or arsenious acid escapes (page 36). The temperature to be employed in the roasting, especially at the commencement, depends upon the character of the assay substance, which should not fuse, though a very slight caking together may be

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allowed; care should be taken, however, that none of it sticks to the dish. Generally, the temperature that a low red-hot muffle affords in its front part, is suitable for the beginning of the roasting. The heat can be raised rapidly or only slowly, and the roasting finished in a shorter or longer time according to the composition of the assay sample.

The presence of *lead*, *arsenic*, and especially *antimony*, makes special caution necessary on account of the easy fusibility of their compounds. Such ores (*e. g. fahlerz*, *bournonite*, etc.), are roasted very gently at first without the addition of coal, and afterwards powdered coal is used instead of graphite, as the ore thus roasts at a lower temperature. If, at the same time, as in many fahlerze, *sulphid of mercury* is contained in the ore, the latter cakes together at a very low temperature, and at a greater heat evolves mercury with such rapidity that mechanical loss occurs. Such ores must be placed in the muffle while it is yet only moderately warm, in order to volatilize the mercury gradually, and be further roasted with coal only after the removal of the mercury. Coke and graphite work almost exclusively and continuously chemically, while charcoal dust has, at the same time, a disintegrating mechanical effect, since generally a large part of the latter is already burned before the ore has reached a temperature at which it can work upon it.

When the roasting ore has ceased to fume, and no longer gives forth any smell of sulphurous acid, it is rubbed up in a brass or cast iron dish (Fig. 18), mixed with about twenty-five pounds of coal dust, and again roasted at a higher temperature till the odorous gases produced have disappeared. The assay is also sometimes calcined with tallow. If the ore is a very difficult one to roast, then, instead of the coal dust, a final addition of forty to sixty pounds of carbonate of ammonia is given, by which the sulphates (even the sulphate of lead) are decomposed with the formation of volatile

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sulphate of ammonia. Generally, a second rubbing up suffices. To secure a complete oxydation, it is necessary that the coal should be entirely consumed.

Arsenic can be removed, for the most part, by this roasting; still some basic arsenates are always formed. Antimony is more difficult to remove, and can only be in some measure driven off by careful roasting and frequent rubbing up. It remains behind as antimonates. A residue of both these substances is less injurious than one of sulphur. The latter occasions in the reduction smelting a formation of sulphid of copper, the copper contents of which escape determination.

When no more fumes from the hot assay can be perceived by smell or sight, and the assay powder shows a constant, uniform, dull color, and no more grains with metallic lustre can be seen while rubbing it up, and finally when no more particles of coal or graphite can be detected, the roasting is finished. It has been proposed to add to the assay, when it is partially roasted, a few (ten or less) per cent. of *chlorid of sodium*, to promote the removal of arsenic, sulphur, etc. This addition, whenever it does not accomplish the end in view, can only be injurious when so much salt is added as to cause a closer baking together of the powder, and thereby hinder the access of air. If the ore contains zinc, this is apt to cause a caking together on account of the formation of chlorid of zinc.

Only with a completely roasted assay can it be counted upon that all or as nearly all as possible of the copper has been converted into oxyd, and this must be accomplished if the result of the assay is to be correct. All the copper which remains in the state of sulphid or sulphate is almost wholly lost, as by the later addition of alkaline flux it cannot be at all, or only very incompletely reduced to metallic copper.

If the assay sample contains sulphates which are not converted into oxyds by coal, graphite and carbonate of ammo-

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nia, *e. g.* gypsum, barytes, etc., it must be first smelted to a matte, which is then treated like a raw ore to be roasted. For this purpose one assay centner of ore, one centner of borax-glass, one centner of potash or soda glass, and ten pounds of colophony are well mixed together, the mixture covered over in a small crucible (Fig. 13) with about three centner of chlorid of sodium, the crucible furnished with a cover, and the assay heated for half an hour in the muffle, or three-quarters of an hour in the wind furnace. The earths are thus slagged off, and there results a cupriferous matte in the shape of a button, which is finely pulverized and roasted.

2. *The solvent and reducing fusion.* If the roasted assay, which besides a small quantity of antimonates and arsenates may contain the oxyds of copper, lead, iron, zinc, etc., is subjected to a reduction smelting with simultaneous use of solvent agents (borax, glass), then by a suitable and not too high a temperature the more difficultly reducible oxyds of iron, manganese, zinc, etc., are in great part slagged off, while the oxyd of copper is reduced, together with a small portion of the above oxyds and most of the oxyd of lead, and yields a button of impure copper (black copper) in which also is found almost the whole of the antimony and arsenic of the roasted ore. If too much solvent flux is used, copper also is slagged, which may be known by the red color of the slag produced. With a lack of solvent agents a great part of the foreign oxyds is reduced, and a very impure black copper is formed, whose refining is attended with greater loss. The charging has been well chosen, when with a black or bottle green slag a malleable button with a copper-red fracture is produced. The presence of much lead occasions a slagging of copper, while iron on the other hand protects the copper from it. Arsenic and antimony aid in the collection of the copper, since the black copper is thereby rendered more fusible.

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The fluxes used in the smelting must be free from sulphur and for this reason the chlorid of sodium is employed in the shape of rock salt, or of salt which has been purified by chlorid of barium. Borax and glass are free from sulphur, but a portion of it is often found as sulphate of lime in the argol, as well as in the saltpetre of the black flux, which serves as a reducing and solvent agent for silica and silicates. The black flux is generally composed of two to two and a half of argol and one of saltpetre; it may vary, however, in composition (as it does, for example, in the *Mansfeld* district), according to the richness of the assay sample. With an ore containing less than forty per cent. of copper it may be made with fourteen argol and eight saltpetre; with forty to fifty per cent. of copper, with sixteen argol and eight saltpetre; and with fifty to seventy per cent. of copper, with twenty argol, and eight saltpetre. The more saltpetre is present the more does the copper incline to slag.

Instead of the black flux,—if this contains sulphur—a mixture of one hundred pounds of pure carbonate of potassa, and ten to twelve pounds of flour is used. To one assay centner of the ore, etc., two centner of this flux are taken, the two are well mixed together, with the addition of thirty to fifty pounds of glass, and twenty-five pounds or more of borax, the mixture placed in a suitable crucible (Fig. 16–17), covered over with two to three centner of chlorid of sodium, a small piece of coal placed on the top, and the crucible closed with the foot of an old one.

If black flux is used, the charge for one centner of ore consists of two and a half to three centner of black flux, twenty-five to fifty pounds of borax glass, and fifty pounds or less of glass that is free from lead and arsenic. The ore is rubbed together in a porcelain or serpentine mortar with one-third of the black flux, placed quickly in a crucible, the other two-thirds of black flux added; twenty-five pounds of

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borax, and thirty to fifty pounds of glass spread over it, the whole covered over with two to three centner of chlorid of sodium, and on the top is laid a piece of coal about the size of a half inch cube. The upper layer of black flux prevents the ore from being thrown out of contact with it by the foaming up of the mass consequent upon the reduction. If the piece of coal is taken too large, almost all the chlorid of sodium soaks into it, and the assay is too much denuded of slag. In the absence of coal, copper is apt to slag. Difficultly fusible ores require a smaller addition of glass, as this itself is rather difficultly fusible. For the better collection of the copper, with richer ores, an addition of five to fifteen per cent. of arsenic is often given: For example, at *Freiberg*, pure chalcopyrite is mixed with fifteen per cent. of arsenic, fifty per cent. of borax, and forty per cent. of glass; erubescite, with fifteen per cent. of arsenic, forty per cent. of borax, and forty per cent. of glass; fahlerz, with ten per cent. of arsenic, twenty-five per cent. of glass, thirty per cent. of borax, and eight per cent. of iron filings. If the ores contain sufficient lead, no addition of arsenic is required. An addition of as high as ten per cent. of iron, with ores that are poor in iron, is very useful both in the reduction smelting and in the subsequent refining of the black copper.

The presence of protoxyd of iron is the safest means to obviate a slagging of the copper, and seems to prevent it to a greater extent, and with more certainty than a change in the ratio of the saltpetre to the argol in the preparation of the black flux, or than the use of a lower and less prolonged temperature in the smelting. Since protoxyd of iron is frequently already present in the roasted assay, an addition of oxyd of iron in the smelting is not always necessary; but the more the proportion of copper in the assay sample increases, the more useful does such an addition prove, so that no error is committed if an addition of from one half to an equal

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weight of pure oxyd of iron, or forge scales, is given to every assay in the smelting, or the assay mixed before the roasting with pure pyrites. The latter diminishes also a loss of silver in the roasting.

Reiterated experience has shown that oxyd of iron prevents the slagging of copper, and, particularly by *Wehrle*, an addition of the same is recommended with substances rich in quartz. Dr. *W. Fuchs* has also drawn attention to this, and by his experiments is led to the conclusion, that a weight of protoxyd of iron equal to that of the black flux can unite with the potassa of the black flux to a chemical compound of the formula 2 Fe O, K O, and that if so much oxyd of iron is added to the assay that Fe O, K O is formed, the copper is made secure from slagging; further, that by the addition of oxyd of iron, the black flux (best made from two saltpetre and five argol) is rendered more fusible.

Since it has long been known that fusing alkaline carbonate is decomposed by oxyd of copper, it must be admitted that oxyd of iron can separate oxyd of copper from its combination with alkali, though this separation may not perhaps be wholly complete.

The assays are exposed to a yellowish white heat for half an hour to an hour in the muffle or wind furnace (in the *Unterharz*, ore and matte assays are allowed to remain in the wind furnace thirteen minutes, and slag assays a quarter of an hour after the fire is well ignited), and when the muffle furnace is used, glowing coals are laid before the crucibles about half-way up to their tops. The contents of the crucibles must be completely fused.

With an assay that has succeeded well (that is, with proper charging and temperature), neither the salt covering nor the slag is reddened with suboxyd of copper. The slag is blackish green from protoxyd of iron, glassy, uniform, and easily snaps in pieces. With a red, and therefore cupriferous slag, either

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the temperature was too high or too long continued, or too little coal, or too much borax and glass present, or the assay too difficultly fusible, which last may be known from the appearance of the heterogeneous, porous slag. Unburned coal must remain on the salt, and at the bottom of the crucible must be found a well fused button of a red or more grayish color according to its purity. If there is found between the copper button and the slag a brittle crust or layer of matte, the roasting was not complete, and the assay is to be thrown away.

Only when substances are to be examined which contain only the sulphids of iron and copper, and besides have but little or no earthy gang, provided too that the quantity of copper is not very small, can a copper button be obtained by roasting and reduction smelting with a well-proportioned mixture whose weight shall give the contents of the ore with sufficient accuracy. But the metallic button obtained must then, with a slag that is free from copper, have all the characteristics of pure copper, must upon its surface as well as in the fracture be pure copper red, and be capable of being hammered without breaking or cracking.

If the color and malleability of the copper button prove that the impurities cannot amount to over one to three per cent. of the weight of the copper, a further refining is omitted on account of the loss thereby occurring. (Mansfeld copper mattes.)

All metallic oxyds still present in the roasted assay sample, which are as easily reduced as oxyd of copper, and whose metals are fusible at the temperature used, either by themselves or when alloyed with copper, pass into the copper as it separates out. In all cases, therefore, when the roasted assay still contains such metals, among which belong lead, bismuth, tin, cobalt, nickel, antimony, arsenic, etc., there can be no pure copper produced, and the copper then obtained is designated by the name of *black* copper. This black copper must

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then, by a further, third operation, be freed from these foreign ingredients, to which, if the roasting was not exceedingly thorough, sulphur may also be added.

3. *The refining of the copper on the cupel or on the refining dish.* This operation aims at the removal of the foreign ingredients from the black copper.

For this purpose the copper is brought into fusion and access of air allowed. Thus the constituents of the black copper, which are more easily oxydized than copper, namely phosphorus, sulphur, arsenic, antimony, lead, iron, bismuth, zinc, etc., are next converted into oxyds, and may be removed as such. A partial oxydation of the copper at the same time, however, cannot be entirely avoided here; and, moreover, when it is attempted to prevent too great an oxydation of the copper, considerable traces of the substances named above are apt to remain behind in the refined copper. From other metals, namely from gold, silver, nickel, cobalt, etc., the copper cannot be freed at all, or only imperfectly so, by this method.

This is the reason of the imperfection of this mode of refining, and, therefore, of all methods of assaying which involve it. The most practised assayer, with all his skill and experience, cannot entirely remove this imperfection. This assay, however, none the less deserves to be used, for with acquired practice it yields a result in a *shorter time*, though it be but more or less approximately correct, than it is possible to obtain one in the wet way. Moreover, rightly conducted assays, compared by the differences usually occurring between them, remain always, or nearly so, quite as reliable as many other metal assays in the dry way, *e.g.* the lead assay.

The assay is in general considered as successful with rich and medium ores, when with correct management the weight of two duplicate assays does not differ by more than one pound.

This refining is performed in different ways.

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a. Refining upon the refining dish. This method is the one most frequently chosen in *Germany*, *e. g.* at *Freiberg*, and at the *Victor Frederic smelting-house*, and also in *Hungary*. It is especially applicable when the black copper does not contain very much lead, and is the more reliable the purer the black copper already is.

By this method indeed an oxydation of the copper cannot be wholly prevented, but under favorable circumstances the loss thus occurring is vanishingly small. In *Freiberg* the copper button, with as little borax as possible, generally an equal weight, wrapped in a cornet of letter-paper, is placed on the very flat, white-hot dish (Figs. 13–14), surrounded by glowing coals, and fused quickly at as high a temperature as possible. A slow fusion occasions oxydation and slagging of the copper. If black copper, which contains neither arsenic, antimony, nor lead, is to be examined, then to a fifty pound assay, five to ten per cent. of lead and thirty to fifty per cent. of borax, as may be required, are added, in which case the borax is generally fused first on the white-hot dish, then the copper, and afterwards the lead added. If the copper to be refined is not in a single piece, then, in order to avoid loss, it is never placed on the dish at the same time with the borax, but only after the intumescence of the latter has ceased. A black copper containing sulphur sparkles when placed on the dish. Cornets of weighed lead and borax must always be at hand to add in case of necessity.

As soon as the copper shows a convex, perfectly clear surface, and is surrounded by a thinly fluid ring of borax slag, the mouth of the muffle is slightly opened to give access to the oxygen necessary for the oxydation. If the copper is not clear, but covered with a black crust, while at the same time the muffle is white-hot, the operator tries adding borax. If this alone does not help the matter, a cornet of lead is added, and the heat increased if possible, when the black copper soon

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presents a clear surface. Very impure black copper with only forty to fifty per cent. of copper, is placed on the dish at first with a large quantity of borax only, without lead, and the latter added only when the copper is sufficiently refined. Special care must now be taken that the temperature does not sink too low. If *lead* is present fumes of it rise at this period. A portion of the lead goes into the slag. *Arsenic* mostly passes off in fumes; a portion of it, however, remains in the slag as arsenate of iron. *Antimony* behaves similarly, only it is more obstinately retained by the copper. *Nickel* is the most difficult to scorify, and can only be slagged by a large addition of lead, and in consequence of this, with a considerable loss of copper. If too little borax is present the slag is apt to become stiff, or solidify.

When the copper is nearly refined, it "brightens" like silver, only less distinctly; the "brightening" is particularly to be seen at the lower edge of the metal. In the presence of antimony and arsenic, the "brightening" is less distinct than with lead, but it becomes so also with the latter when the buttons are small. In the latter case the assay is assumed to be done, when it no longer fumes. The temperature must, at the instant of "brightening," be exactly at the point at which the copper solidifies, since otherwise it would continue to oxydize; but good care must be taken that the copper does not solidify too soon. It shows in the "brightening" a peculiar green color. The assay is now removed from the furnace, carefully quenched in water, and freed from the slag. The buttons should not differ by more than one to two per cent. in weight, and the value is stated only in whole pounds through all degrees of richness.

In a good assay the button has the pure copper color, is ductile, and uniformly granular and rose-red in the fracture. A button not sufficiently refined is red exteriorly, but the fracture is gray; an over refined one, dark red exteriorly and

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brittle, the fracture more smooth than granular, and with a high over refining, even laminated, moreover the slag is then red. With proper refining the slag is blackish green from the presence of iron. If lead was present, the slag is greenish blue at the edges from iron, nearer the button it is yellowish red from $Pb\,O + Cu_2\,O$, and at the button itself suboxyd of copper appears. The yellowish red color must not be confounded with that of the basic arsenate of iron, which forms copper red spangles on the surface of a slag that is saturated with it. Since the adding of lead involves an unavoidable loss of copper, an addition is necessary to the amount of copper found, in order to learn the correct contents of the black copper. Empirically, to every ten pounds of metal slagged off (from the black copper and the lead added) one pound of copper is reckoned as also slagged. In many localities for every five pounds of loss (of the black copper) one pound more of copper is reckoned. If there is a lack of borax in the refining, more may be added in the process. If the dish then becomes too full, it is cooled in water, the copper freed from the slag, and again mixed with borax on a new dish. But then a loss of copper is more apt to occur, as most of the iron, which otherwise protects the copper from slagging, is already slagged off. It is therefore sought in preference to get through, with a single operation.

If much arsenate of iron forms which begins to make the slag stiff, no more borax can be added, as the assay is thereby completely chilled and cannot be again rendered fluid. In such a case the assay must be freed from the slag. A new addition of borax, therefore, should only be given in the commencement, while the slag is yet entirely fluid and the button is not yet clear. When the button once becomes clear, a further addition of borax is seldom necessary if the furnace is kept hot enough. Only very impure black coppers do not then refine with a single operation.

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Plumbiferous black copper is already copper-colored, has a certain softness and quickly refines. Arsenical black copper refines more slowly, requires more borax on account of the iron it contains, and never gives a refined copper of a handsome red color. So long as it is not yet refined, if the heat is high enough it is movable on the dish. With very arsenical copper, if the heat is very strong, a blue arsenic flame bursts forth, which lifts the button. A constant blue halo of burning arsenic is often seen.

Gold and silver remain in the copper, and must be taken account of, when they amount to one-half per cent. Much silver makes the copper white. Generally, only two assays are carried on at once; however, with proper attention four assays may be made at the same time.

b. Refining on the cupel.—This method has been in use here and there, *e. g.* at the *Oberharz* and *Unterharz* smelting works, since the time of *Schülter*. It is by no means more accurate than the above, but is, perhaps, the most suitable one for very plumbiferous black copper.

A quantity of pure copper equal in weight to the black copper is weighed out, while two cupels are brought to a white heat in the muffle of the assay furnace. Upon each of the cupels an equal weight of pure lead is placed, and when this has begun to "drive," the black copper is placed on one cupel and the pure copper on the other, whereupon the muffle is again closed till the alloy on the cupels once more "drives" well. Sometimes (as at the *Unterharz*) half of the lead is placed on the cupel with the copper, and as soon as this is red-hot, the other half of the lead added. The quantity of lead to be used depends upon the character of the black copper; if this is very plumbiferous, an equal weight of lead may suffice; if the black copper is almost or entirely free from lead, and is also impure, two and a half to four parts by weight of lead must be added (at the *Unterharz*, for example, four parts of

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lead are taken). During the "driving," in which the muffle is fully one half opened, without however closing the draft of the furnace, a sufficient heat is to be secured, and it must be especially seen to that both cupels remain equally hot, so that the burning away of the copper may be as nearly equal as possible on the two. The higher the heat in the "driving," the purer does the copper become, and the rounder is its form. The "brightening" of the assay is somewhat more distinct than in the refining on the refining dish. As soon as it has ensued, a spoonful of coal dust or borax is poured over the cupels in the muffle. They are then immediately taken out of the furnace and cooled in water. The indications of the refinement of the copper are the same as above; it is difficult, however, to obtain buttons wholly free from lead. The simultaneous and similarly conducted cupellation of a quantity of pure copper equal in weight to the black copper, with the assay, is intended to make a calculation possible of the quantity of copper, which the black copper has lost by scorification. What the pure copper has lost in weight is added to the weight of refined copper obtained from the black copper. An example will make this clearer. Let the black copper weigh seventy-five pounds. Seventy-five pounds then of pure copper may be cupelled with $75 \times 3 = 225$ pounds of pure lead, and sixty pounds of copper be recovered from it, so that the copper consumed has amounted to $75 - 60 = 15$ pounds. Let the black copper, likewise cupelled with two hundred and twenty-five pounds of lead, have yielded forty pounds of refined copper; then the quantity of copper contained in the seventy-five pounds of black copper amounts to $40 + 15 = 55$ pounds, which is the amount to be stated, if the black copper did not contain lead. If, however, the black copper is very rich in lead, a second correction is also made. The difference, $75 - 55 = 20$ pounds, is considered as lead. Now, as in the assay with pure copper two hundred and twenty-five pounds

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of lead have slagged fifteen pounds of copper; these twenty pounds of lead are assumed to have slagged $\frac{20 \cdot 15}{225} = 1\frac{1}{3}$ pounds more of copper. The quantity of copper to be reported, therefore, amounts to $40 + 15 + 1\frac{1}{3} = 56\frac{1}{3}$ pounds.

If the black copper is so much contaminated with lead that by refining in the manner specified no copper would be obtained from it, an equal weight of pure copper is added to it, and a double weight of pure copper simultaneously cupelled upon the second cupel. For example, let the black copper weigh seventy-five pounds; then seventy-five pounds of pure copper are added to it, and cupelled with $2 \times 75 \times 3 = 450$ pounds of lead. On the other cupel, $75 \times 2 = 150$ pounds of pure copper are cupelled with four hundred and fifty pounds of lead. The calculation is made as above, only the seventy-five pounds of copper added are finally again deducted. If the quantity of lead to be added is diminished, this must be done equally in the actual assay and the controlling one.

2. *English copper assay.*

One centner of ore (about one ounce or $26\frac{2}{3}$ grammes) is mixed according to its character with borax, fluor spar or lime, covered with salt in a crucible, fused in a wind furnace, and the fluid mass then poured out, and sprinkled with water, whereupon the slag separates easily from the matte formed. If the slag contains particles of matte, it is smelted again. The pulverized matte is carefully roasted, with frequent stirring with an iron rod, in a fusion crucible, in the wind furnace, in which crucible it is afterwards smelted with borax, argol and saltpetre to black copper.

In *Cornwall*, according to *Karsten*, the following method is in use:—

The pulverized and finely sifted sample of ore is mixed with one to one and a half times its weight of ordinary glass,

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which only needs to be free from lead or arsenic; with twenty-five to fifty per cent. of saltpetre, and fifty per cent. of borax-glass, the mixture placed in a clay crucible, covered with decrepitated chlorid of sodium, and the crucible, provided with a well-fitting cover, exposed to a strong fusion heat. After cooling, the crucible is broken, and the button of black copper detached from the slag. Instead of the ordinary glass, an addition of fluor spar and lime is often employed. The object of these fluxes is simply to slag the stony gang of the assay ore, and in combination with the borax-glass to form a perfectly fluid slag, so that the particles of copper reduced by the saltpetre from the copper pyrites, &c., may sink to the bottom and unite into a single button. If the slag is too infusible, many globules of copper remain behind, and such assays are considered as having miscarried, though the slag must always be smelted again, the particulars for which follow later in the directions for refining. By this method a tolerably pure button of copper is produced, though it still retains some sulphur, and though a portion of suboxyd of copper is also slagged, since the saltpetre cannot work with entire uniformity.

This mode of assaying is generally applicable only where the copper is found in the ore as sulphid, since all copper present as oxyd, whether free or combined with acids, would be carried into the slag.

The method of refining in use in *Cornwall*, and generally in English copper-smelting works, consists in placing the button of black copper, previously flattened out to a thin plate, in an already red-hot crucible, and as soon as it is fused immediately covering it with raw white flux. A portion of decrepitated chlorid of sodium is also added as a covering. A violent foaming is thus produced. As soon as the mass flows quietly, it is poured into a metallic mould that has been previously rubbed with grease. When it has so far stiffened

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that it can be lifted from the mould with the tongs, it is cooled in water in order to crack the copper button from the slag. The purity of the copper button may be known from its capability of being flattened out without much cracking at the edges, etc. If the indications of purity are not present, the refining process must be repeated, which sometimes happens for the third and fourth time. The foreign ingredients are oxydized and thus removed by the saltpetre in the white flux. But the resulting slag still contains oxydized copper, and is, therefore, together with the slag from the reduction smelting (the ore may have been assayed in the raw or roasted state, page 66), rubbed fine in an iron mortar, mixed with an equal weight of argol, and some pulverized coke, placed in a crucible, covered with salt, and fused at a strong heat. The little globule of black copper which, after the cooling and breaking of the crucible, is found under the slag, is refined in the same way as the black copper from the first reduction smelting, and the button of pure copper added to that obtained from the principal assay, in order to learn the whole amount of copper in the ore as given by the assay.

At the *Elbe copper refinery* at Hamburg, the refining smelting with borax is repeated in a crucible in the wind furnace till the copper assumes the proper color and malleability.

The English copper assay, which is adapted to the English reverberatory furnace process, is accompanied by a considerable loss of copper, particularly in the refining smelting, and is suitable throughout only for pure ores, especially those free from lead.

3. *Plattner's copper assay.*

Plattner has given a systematic method for ascertaining the quantity of *lead*, *bismuth*, *cobalt*, *nickel*, and *copper* to be found in ores, etc., which will be further considered in the

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treatment of the nickel and cobalt assays. (See Bodemann's Probierkunst, pages 433 and 451, etc.)

B. *Assays for poor ores and products.*

1. *Concentration fusion.*

Five to ten centner and more of the unroasted ore are mixed with fifteen to twenty per cent. of iron pyrites free from copper, in case pyrites is not already present in the ore, and the assay smelted with an addition of fifty to one hundred per cent. of borax, under a thick layer of chlorid of sodium in a clay crucible at an incipient white heat. By this process a button of crude matte is obtained, in which the copper of the assay sample is found concentrated as sulphid of copper. This crude matte is weighed, and then first subjected to a copper assay by roasting, reduction smelting, etc. If several assay centner have been taken for the concentration smelting, the final proportion of copper found is calculated accordingly.

A slagging of copper is indeed seldom entirely avoided by this concentration smelting, but the loss of copper is generally less than if such poor ores were at once, without any previous work, subjected to the ordinary process in the dry way, which would sometimes yield no button of copper at all, since the little copper in the ore is lost in the slag.

According to *Fuchs*, for the most complete prevention possible of a loss of metal, and for the purifying of the copper, the well roasted ore is placed in an assay crucible while still hot, with twenty per cent. of pyrites and twenty per cent. of sulphur, covered with powdered glass and some vitrified borax, and smelted to matte.

2. *Fusion with collecting agents.*

With *poor* and *impure* ores, if the ordinary method is used, errors are very apt to arise from the infusibility of the

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ore, and from the basic nature of the suboxyd of copper, which, especially in the presence of silica, is very much inclined to slag. In such cases, as practised in *Freiberg*, lead, litharge, arsenic, antimony, arsenious acid, or oxyd of antimony, is added for the collection of the copper while smelting to black c pper. These fluxes have their advantages, but also their disadvantages. Five to fifteen per cent. of *lead* or *litharge* gives with copper an easily fusible alloy, which collects better together, but also carries copper into the slag, which consequently becomes red. If the result of experience is taken as a basis, that, in the refining smelting, ten pounds of lead slag, one pound of copper, then if five per cent. of lead are added to an ore with one per cent. of copper, only half a pound of copper is obtained, and with ten per cent. of lead no copper at all would be obtained. The intimate mixture of the lead with the ore has also its difficulties, and therefore it is better in this connexion to use litharge.

By an addition of *arsenic*, *antimony*, *arsenious acid*, or *oxyd of antimony*, easily fusible compounds of arsenic and antimony with copper are obtained, the mixing can be accomplished more thoroughly than with lead, and for poor ores, such an addition is more suitable than one of lead. On account of danger in dealing with arsenious acid, it is best to use metallic arsenic, which does less harm in the refining than antimony. In this operation, indeed, neither of the two is entirely removed from the copper, and they impart some brittleness to it, and a grayish color to the fracture. The assayer may, however, be satisfied with the result of an assay treated with arsenic.

II.—OXYDIZED ORES AND PRODUCTS.

Oxydized copper ores and products are—

1. Without previous roasting, subjected to a solvent and

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reducing fusion, and the black copper thus produced, refined if necessary (richer ores and products, *e. g.* red copper, malachite, refinery slags, etc.).

2. After previous roasting, smelted to black copper, *e. g.* sulphate of copper, copper ores which contain arsenic acid, antimonic acid, etc., ores imperfectly roasted in the large way many copper ore slags, cement copper slimes, which may contain basic sulphate and arsenate of iron, etc. The roasting is performed with an addition of coal dust or graphite, and finished, if necessary, with carbonate of ammonia.

3. Smelted to black copper with collecting agents (lead or arsenic). Poor oxydized copper ores, especially the quartzose ones, must always be treated in this way. For example, poor copper ore with chalybite and basic gang without silica is mixed with ten per cent. of arsenic, thirty to forty per cent. of borax, and twenty to twenty-five per cent. of glass; if it contains pyrites, mispickel, quartz, and calc-spar, with twelve per cent. of arsenic, thirty per cent. of borax, and thirty per cent. of glass, besides black flux; ferriferous, quartzose malachite, with ten per cent. of arsenic, sixty per cent. of borax, and fifteen per cent. of glass. If poor oxydized ores are free from iron, ten to twenty per cent. of oxyd of iron is added. Also, richer oxydized substances are advantageously mixed with collecting agents, *e. g.* refining slag, with five per cent. of arsenic, thirty per cent. of borax, and thirty per cent. of glass.

4. Subjected to a concentration fusion, with twenty to twenty-five per cent. of pyrites free from copper and twenty per cent. of sulphur, one hundred per cent. of vitrified borax, one hundred per cent. of glass, and twenty to twenty-five per cent. of colophony with a covering of salt, and the resulting matte treated like a sulphuretted ore. The ore is placed on top of the pyrites and sulphur, and covered over with the fluxes, &c.

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III.—COPPER ALLOYS.

But very few copper alloys can be refined by the above process. For the *black copper* produced by the copper smelting-house process, everything is observed which was prescribed for the refining of the buttons resulting from the reduction smelting. If the refining is to be done on the cupel, one or more rarely two centner are weighed out for the assay. *Cupriferous lead* is refined on the cupel. Two centner of the cupriferous lead and half a centner of pure copper are placed on one cupel, and on the other, two centner of pure lead and half a centner of pure copper, and the two are cupelled at an equal heat. If now, for example, thirty-six pounds of copper have been obtained on the first cupel, and twenty-seven pounds on the second, then in the two centner of the assay substance there were contained 36 — 27 = 9 pounds, or four and a half per cent. of copper.

Heine gives for the examination of the Mansfeld *black copper*, which seldom contains more foreign ingredients than four to seven per cent. of iron, a little sulphur and only traces of zinc, cobalt, nickel, lead, and phosphorus (the whole amount of the substances last named is not generally over one per cent.), the following directions.

One or half an assay centner of the black copper in filings is weighed out in duplicate, and placed in the muffle, at first with a gentle, then with a stronger heat, and with frequent rubbing up, until all the copper appears black and changed to oxyd and no more grains can be felt with the pestle. The roasted assay is now mixed with two to three centner of black flux and one to one and a half centner of glass free from lead and arsenic, the charge placed in a crucible for assaying copper, covered with salt, and smelted in the wind furnace. The black flux for this assay must consist of at least twenty parts of argol to eight parts of saltpetre, since with a smaller

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quantity of argol red slags are generally produced. Should this still be the case, six to eight assay pounds of coal dust are added to the charge. *Heine* obtained in this way a copper, which he considered quite as well refined as that produced by the preceding processes.

These directions may, perhaps, deserve to be followed with black copper similar to this, as they allow us to dispense with the always imperfect refining on the cupel or refining dish; especially if for reasons already explained a portion of pure oxyd of iron or forge scales is mixed with the roasted assay in the smelting, in order the more certainly to avoid the formation of a red slag, which always indicates loss.

The most frequent alloys of copper, i. e. *brass*, *German silver*, *gun metal*, etc., cannot be assayed in a reliable manner in the dry way. German silver, because the nickel could not be removed at all, or only with great difficulty, and the rest because zinc and tin give such difficultly fusible oxyds, that they could not be properly removed in the refining.

In the *alloys of copper with silver*, *gold*, and *platinum*, the copper may be determined from the loss arising from cupellation with lead.

Remarks upon the copper assays in the dry way.

These assays are burdened with various defects. The roasting is an exceedingly tedious process; and only by a gradually increasing temperature, by repeated rubbing up and mixing of the roasting substance with coal dust, graphite or carbonate of ammonia, is it possible to sufficiently remove the sulphur. In the reduction smelting, loss of copper is apt to occur if a correct temperature and a suitable charging are not hit upon. If the fluxes (borax, glass, etc.) are present in too large quantity, copper is slagged; if there is a lack of them, a very impure black copper is produced, with whose diminishing richness in copper, the loss of copper in the refin-

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ing increases. The last mentioned operation is in and of itself imperfect, and on account of the high temperature it requires, and the ever necessary attention of the assayer, very troublesome.

The poorer the substance is in copper, the more unreliable do the results of the assays become.

In all docimastic assays of copper in the dry way, the *silver* or *auriferous silver* contained in the assay sample cannot be removed, and it has generally pretty completely collected in the copper obtained. These copper assays give nowhere any indications whether gold or silver is present or not; and the amount of these metals which may be present must therefore be both sought for and determined by a special assay for them. If they are found, and in sufficiently large quantity, they are deducted from the weight of the copper.

The dry assay is mostly found in practice in smelting works, where even in the hands of less scientifically educated than skilful assayers, with the character of the assay substance once known, and suitable practice in following out the separate manipulations, it gives results which suffice for the business of working copper in the large way.

Section II.

B. COPPER ASSAYING IN THE WET WAY.

I.—ASSAYS FOR SUBSTANCES RICH IN COPPER.

A. *Modified Swedish copper assay in use at the Oberharz smelting works.*

This consists in general, in bringing the cupriferous substance (ore, metallurgical product, alloy, etc.) into solution and precipitating the copper with iron. This was generally accomplished formerly by evaporating the finely rubbed assay sample to dryness with sulphuric acid, adding some acid to

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the dry mass, lixiviating it, and gradually precipitating the copper from the somewhat warmed solution, with an iron wire about one quarter of an inch thick.

This management has several defects. Many products are disintegrated with difficulty by sulphuric acid, and therefore, the mass that has been evaporated to dryness with it must often be repeatedly treated with acid. The precipitation of the copper lasts from four to eight hours and longer, and so a formation of basic salts which contaminate the copper is apt to occur. This method is therefore time-consuming and unreliable.

These defects are removed by the following method, introduced at my suggestion in the *Oberharz* smelting works.

One assay centner of finely rubbed ore, etc., is warmed in an assay flask or beaker, on the sand-bath, with as little as possible of aqua regia (two parts crude hydrochloric, and one part crude nitric acid), and as soon as the proper decomposition of the assay substance has taken place, in order to expel the nitric acid, evaporated nearly to dryness with a few drops of oil of vitriol. In the presence of nitric acid the copper would be only imperfectly precipitated by iron; the presence of hydrochloric acid does no harm. Also the nitric acid may be destroyed by heating the solution containing it with crystals of protosulphate of iron, only the work then passes off less cleanly than if sulphuric acid is used.

The still damp mass is cautiously moistened with hot water, and filtered into a beaker, the residue no longer containing any particles of ore, etc., is washed out a few times with boiling water (till a drop of the washings no longer deposits a brownish coating of copper on a clean iron wire), the filtrate, about 150 to 160 cubic centimeters, heated nearly to boiling with a few pieces of iron wire about two inches long and two lines thick, till a brownish coating no longer forms on a clean iron wire held in the solution. The approximation to this point

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is indicated by the solution's becoming colorless. Should the mass become dry in the evaporation with sulphuric acid, it is dampened before filtering with a few drops of sulphuric acid, in order to make the basic salts formed soluble. The concentrated solution is not filtered on to the pieces of iron wire, but these are placed in the solution after it is diluted with the washings, because otherwise they become so rapidly and so firmly coated over with copper, that the latter can only with difficulty be separated from them. The pieces of wire are so taken as to correspond in size with the beaker used, and of such a length as to cross one another in it, in order to present as much surface as possible to the direct contact of the fluid.

After the precipitation is ended the beaker is poured full of hot water, which, after some time, is decanted, care being taken that no copper goes with it, the beaker again filled with hot water, a porcelain saucer placed bottom upwards on the top of it, and beaker and saucer then inverted so that the iron wires, together with the copper and some of the fluid, sink into the saucer. When this has taken place completely, the beaker is removed from the saucer by drawing it quickly over the side with the hand, the iron wires freed by rubbing them with the fingers from the copper coating which does not adhere firmly, well rinsed off, and the copper well washed two or three times by decantation with hot water. The decanted fluid may be placed in a beaker and allowed to stand quiet for some time, that it may again deposit any very finely divided copper suspended in it. The latter is not to be confounded with the particles of carbon separated from the iron wires, and which pass off in part in the decanting. Owing to the short time occupied by the precipitation of the copper, few or no particles of carbon and iron are detached from the wires, as in the older assays, and the copper is precipitated with a pure metallic color, without being in the least contaminated by basic salts of iron.

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The damp copper, freed from water as much as possible (if necessary by removing it with blotting paper) is dried at a gentle heat in an atmosphere free from acid vapors until two successive weighings give the same result. An oxydation of the damp copper may be counteracted by adding alcohol to it, and also by covering over the saucer. Overmuch care in the drying is not required, for even at a somewhat higher temperature the increase in weight is but very small, so long as the copper retains its proper color. The precipitated copper should not be allowed to remain too long in contact with free sulphuric acid, since it is oxydized by it.

This process alone, can only be used when in the substance to be examined there are no other metals present (*tin*, *antimony*, *arsenic*, *gold*, *bismuth*) which are likewise thrown down by iron. *Silver*, *lead*, and *mercury* are indeed also precipitated by iron, but these metals can be readily removed. *Silver* and *lead* remain in the insoluble residue, the first as chlorid of silver and the last as sulphate of lead, and may be determined by assaying it after incinerating the filter. *Mercury* (contained for example in many fahlerze) is indeed thrown down with the copper, but is volatilized by igniting the copper in a porcelain crucible or on a roasting dish in the muffle, whereby the copper also passes into pulverulent black oxyd, and after two ignitions is weighed as such. One hundred parts of oxyd of copper contain 79.826 of metallic copper. The oxydation may be promoted by dampening the copper with nitric acid before ignition.

The so-called *copper slate* (Kupferschiefer) must, before treating with aqua regia, be ignited to remove the bitumen. If the substance cannot be completely decomposed by aqua regia (many *slags* for example) it is first fused in the finely pulverized state with about two to two and a half parts of carbonate of potassa or calcined carbonate of soda in a clay crucible at a red heat in the muffle or in a platinum crucible

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over a spirit lamp. If the assay sample contains *lime*, difficultly soluble sulphate of lime is formed, which may however be dissolved out by repeatedly washing the copper with boiling water.

The presence of *iron*, *nickel*, *cobalt*, *manganese*, and *zinc* in the assay substance does no harm, as their sulphates are not decomposed by iron.

While by the older method an assay might last from one to two days, during which time, indeed, as many assays might be simultaneously conducted as the arrangements otherwise allowed, all the operations of this newer method require but from two and a half to three hours, with an ore containing two to seventy per cent. and more of copper.

With respect to the accuracy of the assay, with suitable substances, as the experiments at the *Oberharz* smelting-house and the investigations of *von Hubert* have proved, it leaves nothing more to be desired as a business assay. At the smelting-house alluded to, the different assayers are allowed two per cent. difference, which is however very large.

Mohr has given an analytical accuracy to this assay, by performing all the operations as much as possible in the same vessels, conducting the washing with care, and precipitating the copper with granulated zinc free from carbon, instead of using iron, which liberates coal. As a business assay, however, the Oberharz method is to be preferred on account of its simpler practicability.

If *bismuth*, *gold*, *tin*, *antimony*, or *arsenic* are present in the substance to be assayed, the method described requires different modifications according to whether *arsenic* is present or not. The presence of *bismuth*, which moreover seldom occurs (*e. g.* in many *fahlerze*, *cupreous bismuth*), also necessitates a special assay treatment.

a. Arsenic is not present. One assay centner of the ore, etc., is decomposed at a more or less high temperature by

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nitric acid, so that *gold*, *oxyd of antimony*, and *oxyd of tin* remain in the residue, as also *silver*, if some chlorid of sodium is added to the solution. It is now filtered, the precipitate washed with water, the filtrate evaporated, to expel the nitric acid, and to separate any *lead* that may be present, with sulphuric acid (page 75), and the copper precipitated from the filtrate in the usual way. Mercury, if present, is removed in the manner stated above (page 77).

b. Arsenic is present. One assay centner of ore is decomposed in a beaker or a roomy flask with as little aqua regia as possible, the free acid neutralized with soda, or even supersaturated so that a precipitate separates, and the mass digested with excess of solution of sulphid of sodium for some time (perhaps half to three quarters of an hour) at almost boiling heat. The solution of sulphid of sodium is prepared by igniting and lixiviating a mixture of two parts of anhydrous carbonate of soda and one part of coal dust or flour. To the filtered solution of this salt flowers of sulphur are added in excess, which partially dissolve in it and increase its capacity for dissolving the electro-negative sulphids of *gold*, *antimony*, *arsenic*, and *tin*, by forming with them sulphur salts, while *silver*, *lead*, *copper*, *mercury*, *iron*, *zinc*, *manganese*, *nickel*, and *cobalt* are sulphurized by the solution, but not dissolved. The two groups of metallic sulphids are separated by filtering and the sulphids of the last group, which remain on the filter, well washed with cold water. The finger is then held over the bottom of the funnel, concentrated nitric acid poured on the filter, and the sides of the funnel carefully heated by slowly revolving it over a spirit lamp. The sulphids thus partially dissolve in the acid, but separate completely from the filter, so that by punching a hole through the bottom of it they can without difficulty be washed into a beaker. Here they are completely decomposed by heating with the nitric acid, the latter removed with simultaneous separation of the

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lead, by heating with sulphuric acid, and the process continued as heretofore prescribed (pages 75–76).

c. Bismuth is present. After *gold*, *antimony*, *arsenic*, and *tin* have been removed, if necessary, in the manner prescribed under *a* or *b*, carbonate of ammonia in excess is added to the solution obtained, which contains copper and bismuth. By this the copper is dissolved, while *bismuth*, *lead*, and *mercury* are precipitated as carbonates. After a while the blue copper solution is filtered off, the carbonate of ammonia supersaturated with sulphuric acid, and the copper precipitated from the solution with iron. Should much iron and alumina be contained in the solution that has been freed from gold, antimony, arsenic, and tin, then in the precipitation with carbonate of ammonia a slimy precipitate is formed which may retain much copper. In such a case the solution is evaporated with sulphuric acid, and the copper precipitated in the usual way with iron. Since, however, the copper then contains bismuth and mercury, it must be redissolved in nitric acid, and the solution treated as above with carbonate of ammonia.

Synthetic experiments with substances of most varied composition have proved that this modified assay yields sufficiently correct results as a docimastic assay with ores containing two to seventy per cent. and more of copper. Either the precise percentage of copper weighed out is again obtained, or with the richer ores a difference of at most two per cent. occurs between several assays of one and the same kind.

By means of the *Oberharz* assay and *Heine's* colorimetric assay (page 81) the copper contents of all substances, rich and poor, can be docimastically determined with sufficient accuracy. By the *Oberharz* assay, proportions of two to three per cent. and over are determined, and by *Heine's* mode the lesser ones down to .03 per cent.

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B. *Colorimetric Copper Assays.*

These are based upon the fact that ammonia added in excess to the solutions of salts of copper, produces a beautiful azure blue color, whose intensity depends upon the quantity of copper dissolved. By comparing the shades of blue color in equally thick layers of the dissolved ammoniated assay substance (assay fluid), with a normal or standard ammoniated fluid whose copper contents are known, the quantity of copper in the former can be calculated when its volume is measured.

To *Heine*, the superintendent of the smelting works in *Mansfeld*, belongs the merit of having first successfully employed this reaction for the determination of small percentages of copper, and later it has been also extended by *Jacquelain*, *von Hubert*, and *Müller*, to the determination of larger quantities of copper.

1. *Heine's Colorimetric Method.*

For the docimastic determination of the quantity of copper in bodies poor in this metal, *e. g.* in slags, lead matte, litharge, crude lead, and other plumbiferous metallurgical products, tin, cupelled silver, etc.; in short, in all substances which contain from a trace to about one per cent. or a little more of copper, this method is the most advantageous to be used.

After the assay sample has been reduced to as fine a state of mechanical subdivision as possible, which with slags is best attained by sifting or washing them, one centner (3–4 grammes) of it is weighed out and dissolved or so fully decomposed by a suitable acid that in the residue, which is to be filtered and well washed, no more copper remains behind. For this purpose nitric acid or aqua regia is employed, according to the character and peculiar behavior of the substance, and the nitric acid is concentrated or somewhat diluted, as may be required. The solution is either immediately, or after

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the copper has been first precipitated by hydro-sulphuric acid gas or iron and again dissolved, strongly supersaturated with caustic ammonia, and the precipitate, if any, thereby produced, steeped in the caustic ammonia for a considerable time, and with frequent stirring at a very gentle heat (30°–40° C.), then filtered off and thoroughly washed. According to the quantity of copper present, and according to the degree of dilution, will the solution obtained, which if it should become at all turbid must be once more quickly filtered (*e. g.* with refined and crude lead), appear more or less strongly colored blue. The volume of the solution is measured in graduated vessels, and the intensity of the color compared with and determined from fluids, which have been previously prepared as standard fluids, and which, for a definite volume, contain a definite, accurately weighed quantity of copper, that has been dissolved in nitric acid, precipitated by caustic ammonia, and redissolved in excess of the same. From the measured volume, and the intensity found by comparison, the quantity of copper is then determined by calculation.

Heine proposes standard fluids with one, two, three, and four assay loth of copper in one ounce (two loth, commercial weight) of the ammoniated fluid. These four standard fluids are all-sufficient.

If the French weights and measures are used, standard fluids are taken with .001 .002 .003 .004 grammes of copper to every twenty-five cubic centimetres of the fluid.

The graduated vessels (cylinders) required for the preparation of the standard fluids as well as for the measuring of the assay fluid can be easily prepared by the assayer himself. One quarter of an ounce of water is weighed out a number of times in succession and poured into the cylinder, and each time the height of the fluid is marked in a durable manner on the glass with a diamond, or by etching it with hydrofluoric acid vapors, etc. Also earthen or porcelain measures,

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that are prepared and marked for the volumes that hold one, two, three, four, etc., ounces of water, may be used.

It is not practicable to replace the volumetric measurement by weighing, for the quality and quantity of those substances which are soluble in acids and not precipitated by ammonia, or are again dissolved by it, may vary greatly in the assay.

In the formation of the normal fluids, two assay pounds of chemically pure (galvanic) copper are weighed out on a good balance, dissolved in nitric acid, the solution supersaturated with caustic ammonia, and placed in a graduated cylinder, which is divided to whole, half, and quarter ounce volumes of water, and then water enough is added to bring the fluid to the sixteen ounce mark. The fluid then contains $\frac{64}{16} = 4$ loth of copper per ounce. Six ounces of this four loth solution are then taken, two ounces of water added to it and eight ounces of fluid obtained, with $\frac{24}{8} = 3$ loth of copper to one ounce of water. The two loth solution is formed in a similar way by diluting four ounces of the four loth solution to eight ounces; the one loth, by diluting four ounces of the four loth normal fluid to sixteen ounces. In the measuring of the assay fluid it is estimated within one-eighth of an ounce, which is sufficiently close. If in the dilutions a mistake is actually made of one-sixteenth of an ounce, the maximum of possibility, the error amounts to about two cubic centimetres, which in a whole mass of fluid of 200–500 cubic centimetres has no influence upon the solution that can be detected with the eye.

The preservation of the standard fluids as well as the comparison of the blue assay fluids with them must take place in glass vessels closed with ground glass stoppers. These vessels must have the same form and size, consist of the same colorless glass, and have an equal thickness of glass in the smooth side-walls. The last condition is obtained the surest by grinding. This grinding, however, which notably in-

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creases the cost of the glasses, is not indispensably necessary, if the vessels are carefully formed and blown in a good glass-house. An oblong form is most advantageous for the vessels. They hold about an ounce and a half of fluid, and are about two inches long, two and a half inches high, and one inch wide, with walls about one-eighth of an inch thick.

The glasses are very advantageously formed from an unblemished sheet of plate glass of equal thickness throughout, either by fusing or cementing the sides together and the insertion of a glass or platinum neck. The assayer has in the form of vessel indicated a triple control in the comparison of the assay fluid with the normal solution, according as he looks through the fluid in three different directions.

The digestion of the assay sample with acid may take place in any suitable vessel whatever, a glass flask, a beaker covered with a watch-glass, &c., only no thumping and spirting of the fluid should be possible in the process. The nitric acid, etc., must be added little by little. The time required for this may vary greatly. The solution of *cupelled silver*,* *skimmings*, etc., with nitric acid is finished in a short time; on the other hand, in the examination of difficultly decomposable *slags*, with which concentrated nitric acid or aqua regia will always be used, the digestion often requires to be continued in a warm temperature for two to three times twenty-four hours. The mass must be frequently stirred with a glass rod, because many slags decompose rapidly with evolution of heat, form a thick jelly, and deposit a crust on the bottom of the glass. Sub-, singulo-, and bi-silicate slags, mostly decompose readily, higher silicates resist complete decomposition by aqua regia, and then a preliminary solvent ignition or fusion with carbonate of potassa or calcined carbonate of

* With cupelled silver, after dissolving in nitric acid, the silver may be precipitated with chlorid of sodium, the chlorid of silver filtered, washed, and the solution then mixed with caustic ammonia.

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soda; or better, a mixture of both is necessary, precisely in the manner given in the wet assay of copper, page 77. Here also it does no harm if some of the substance of the crucible remains adhering to it.

The decomposition of the slags by acid is complete when in the stirring with a glass rod no more grating can be perceived.

After hot water has been added to the decomposed assay, the residue is collected on a filter, well washed out, without diluting the filtrate too largely, and the copper precipitated from the solution if necessary with hydrosulphuric acid gas, especially when a notable quantity of alumina and iron is present, whose slimy precipitates from the immediate precipitation with ammonia always retain copper. This precipitation of the copper has also the advantage that, as cobalt and nickel do not precipitate with it, the coloring effects which they would produce if present are removed. Since the sulphid of copper requires for its solution but a few drops of nitric acid, in the succeeding treatment of the solution with ammonia, but a small quantity of ammoniacal salt is formed, and the specific gravity of the colored fluid varies but very little from that of water and the normal solution. With the increase of the specific gravity of the assay solution, its volume is considerably increased, and therefore it gives too large a measure in the direct precipitation with ammonia. If the precipitation with hydrosulphuric acid gas is completed in four to six hours, the sulphid of copper is filtered out, thoroughly washed with cold water containing hydrosulphuric acid, the filter dried, ignited in a porcelain crucible, the oxyd of copper formed, warmed with a few drops of nitric acid or aqua regia, supersaturated with ammonia, filtered, and well washed till the washings are no longer tinged bluish.

A precipitation of the copper with iron wire (page 75) from a solution evaporated with sulphuric acid, and a re-solution of the copper in nitric acid, consumes less time. If the copper

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is not previously precipitated, errors of some thirty per cent. and more of the whole amount of copper may occur. By repeated solution of the iron precipitate and precipitation with ammonia, all the copper cannot, however, be extracted.

In the examination of *litharge*, the solution in nitric acid may be dispensed with. The oxyd of copper can be at once extracted from it with caustic ammonia; however, the litharge and ammonia must then be allowed to work at least twenty-four hours on each other, with very diligent stirring, and moreover the litharge must be rubbed very fine.

The ammoniacal solution obtained from the assay is now well stirred, so that it may mix with perfect uniformity with the last washings; then, either the whole or a part of it is placed in a clean assay glass, and compared with the standard fluids in similarly formed glass vessels standing on a sheet of white paper. Should it correspond with none of them in the intensity of its color, the whole of the fluid is diluted somewhat with water, until this is the case. Its volume is thereupon measured in the glass vessel graduated to ounces, etc., and noted. For a check, the dilution may be carried still farther till the color of the assay corresponds to the next more faintly colored standard fluid, and then the increased volume be measured anew. This might perhaps be still again repeated, but it becomes more and more uncertain. The calculation of the percentage of copper from the intensity and the volume found, then presents no further difficulty.

Suppose that the assay fluid agrees with the normal solution of four loth of copper to the ounce of water, and its quantity amounts to five ounces, then the quantity of copper in the centner of the assay substance is $5 \times 4 = 20$ loth. This fluid further diluted till it equals the normal solution with three loth of copper, must measure six and two-third ounces if the obtained value of twenty loth is to be confirmed.

According to *Heine's* experiments, the possible error of

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observation in the comparison and measurement described, amounts as a maximum with the stronger normal solutions (with sixteen loth and over) to three quarters to one loth, with the weaker ones to scarcely half a loth of copper. In a centner of the assay substance, one loth of copper =.03 per cent. can still be determined with certainty.

Le Play determined in finely pulverized and carefully washed copper slags, the copper in one gramme of the poorest slags to within half a milligramme, and of the richest slags to within one milligramme, by using twenty-six standard fluids with various percentages of copper in cylindrical vessels. The comparison of colors in round vessels is more uncertain than in oblong ones, since in the former the light is dissipated and shadows are produced.

If a substance contains so little copper that the fluid does not equal the most faintly colored standard fluid in intensity of color, the assayer must endeavor to remedy the matter by *evaporating* till this is the case. An evaporation is, however, avoided if possible, first because of the loss of time, and also because other precipitations, carbonate of lime, etc., are apt to be caused by it, and because, when it has to be continued too long, so much ammonia is very apt to be volatilized, that a new addition of it becomes necessary.

This method of assaying soon finds the limits of its accuracy in an increasing percentage of copper in the assay sample, since with fluids rich in copper and therefore strongly colored blue, the errors of observation soon amount to several loth. And to seek then to better oneself by diluting largely, yields no more accurate results, since a small error of observation in determining the intensity of the color, is so much the more multiplied in the calculation of the value by the greater number of the ounces.

If *nickel* is contained in the assay substance, the assay cannot be conducted in the way prescribed, since the nickel is

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extracted by the acids, and dissolves also in caustic ammonia with a blue color. The assay may also become uncertain from the presence of much *manganese*, *cobalt*, or *chromium*, since they render the hue of the blue color dingy. *Chromium* may be completely removed by a slight boiling of the ammoniacal fluid; not so cobalt. The presence of *vanadium* or *molybdenum* does no harm.

If *nickel*, or much *cobalt* and *manganese* are contained in the assay substance, the solution obtained by acids and filtered, though not further diluted, must first be decomposed by metallic iron. What is thrown down by the iron is collected on a small filter, washed thoroughly, and then, together with the filter, treated with dilute nitric acid. When the copper is all dissolved, this solution is supersaturated with caustic ammonia and then managed as above. With higher percentages of copper the process of the Swedish copper assay is used for determining the value. The precipitation of the copper may also be performed with hydrosulphuric acid gas.

Le Play removes the injurious influence of manganese, nickel, and cobalt, by allowing the green or violet-colored ammoniacal solution to stand open to the air for several weeks in a moderately warmed drying furnace, whereby a few variously colored gelatinous flocks are gradually deposited, and the fluid, after the addition of a few drops of ammonia, then becomes pure blue.

According to *Jacquelain* and *von Hubert*, nickel and cobalt are in a simple way rendered perfectly harmless by gradually adding white pulverized marble to the solution of the assay substance until the effervescence ceases, and then warming the whole on the sand bath, whereby all the copper is perfectly precipitated as carbonate, while nickel and cobalt remain dissolved. It is now filtered, washed, the residue dissolved in nitric acid, and the solution treated, as already explained, with ammonia. By the addition of carbonate of

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potassa to the ammoniacal fluid, and heating, all the manganese precipitates, while the copper remains dissolved in the excess of ammonia, and can be separated from the manganese precipitate by filtration. The manganese must have been present as oxyd in the original solution, in order that the precipitation by carbonate of potassa may be perfect.

The assayer may convince himself whether *nickel* or *cobalt* is present, by slightly supersaturating a blue ammoniacal solution, obtained by the ordinary process of assaying, with hydrochloric or sulphuric acid, then precipitating the copper *completely* with iron, filtering the residual solution, concentrating somewhat if necessary, and now supersaturating with ammonia. If the fluid then remains colorless, neither of the two metals is present; a blue color indicates nickel, a red one cobalt.

Sometimes the normal solutions which when freshly prepared appear azure blue, assume a greenish hue, which renders the comparison difficult if not impossible. Nitrate of copper produces with ammonia a pure azure blue, sulphate of copper a lilac color, and chlorid of copper greenish hues. Sulphuric and hydrochloric acid are therefore avoided as much as possible in the solution. But nevertheless, an assay fluid may sometimes, *e. g.* by standing some time in the air or by slow filtration, become green, in which case the color is destroyed by a few drops of nitric acid, and ammonia added anew. But sometimes also the greenish color disappears, if the solution stands in a covered vessel in the air, or by the addition of a few drops of red ammonio-oxyd of cobalt.

According to *Müller* also, the color stands in the closest connection with the quantity of ammonia employed, and it therefore leads to greater accuracy in the assay, if a titrated solution of ammonia is used, and the volume of ammoniacal fluid noted, which, after neutralization of the residual free

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acid, is used for the solution of the copper. The solution appears more intense when viewed with a gray background than with a white one. A greenish blue coloring becomes the more noticeable, the greater is the excess of ammonia, or the more ammoniacal salts are in the solution.

2. *Jacquelain's and von Hubert's colorimetric assays.*

Heine's method, for the reasons stated, is suitable only for the determination of small quantities of copper. *Jacquelain* has extended it to the examination of all cupriferous substances, and this process has been further perfected by *von Hubert.* According to the latter, a solution of any cupriferous accurately weighed substance is prepared, mixed with ammonia in excess, the ammoniacal solution (assay solution) measured at a definite volume, and a small, likewise measured portion of the measured solution, diluted with water, until its blue color shows an equal intensity with the blue color of another solution (normal solution) also cupriferous and ammoniacal, whose copper contents are known once for all. Then, from the quantity of water added, in order to make the two fluids equal to each other in the intensity of their blue colors, the amount of copper in the substance under examination can be determined by calculation.

The normal solution is prepared by dissolving .5 of a gramme of chemically pure copper in dilute nitric acid, adding ammonia in excess, and diluting with distilled water until the whole at 12° C. amounts to one litre = 1000 cubic centimetres. The solution is filtered, and preserved in a flask provided with a glass stopper ground in to fit it.

For the preparation of the assay fluid, with substances whose percentage of copper ranges from 1.5 to the highest per cent, two grammes, and with the poorer substances five grammes, are brought into ammoniacal solution with the precautions specified in *Heine's* assay (page 84). This solution,

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with over five per cent. of copper, is measured at two hundred cubic centimetres, with two to five per cent. of copper at one hundred and fifty cubic centimetres, and with two per cent. and under, at one hundred; and also, as may be required, at 90, 80, 60, 50 c. c., according to the intensity of the fluid. Only with an extremely small quantity of copper is the assay fluid evaporated to a smaller volume, in order to be able to conduct the colorimetric test with accuracy.

The comparison of the intensity of color of the assay fluid with the normal fluid is accomplished in two different ways, according as the former, when measured at a definite volume, is darker or lighter than the latter. This can be seen if a small arbitrary portion of each is poured into a glass tube of nine millimetres interior diameter, twelve centimetres in length, and uniform thickness, and the two tubes are held in parallel positions over a piece of white paper so that they rest firmly on it, and are inclined to it at an angle of about 45°, and direct light falls upon them. Shadow should not fall upon the tubes.

a. *The assay fluid is darker than the normal solution.* By means of a pipette, five cubic centimetres of the normal solution are placed in a glass tube closed at the bottom and not graduated, and seven millimetres in interior diameter and twelve centimetres long. Since 1000 c. c. of the normal solution contain .5 of a gramme of copper, five cubic centimetres contain exactly .0025 and the ratio 5 : .0025 expresses once for all the known proportion of copper in the normal solution.

Five cubic centimetres of the definitely measured assay fluid are now also placed in a beaker and gradually diluted with water till they show the same intensity of color as the normal solution. In the comparison the assay fluid must be in a similar tube to that containing the normal solution. With richer proportions a greater accuracy is attained in this comparison, if the assay fluid is so far diluted that its intensity still appears

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as little as possible darker than that of the normal solution, and then water added carefully, and drop by drop, till its intensity is judged as little as possible lighter than that of the normal solution, whereupon the mean of the two volumes noted is taken as the correct value. The measuring of the diluted assay fluid is performed in glass tubes of nine millimetres interior diameter and fifty centimetres in length, which from their lower closed end to the circular mark designated by O hold exactly five cubic centimetres, and from O upwards are divided into cubic centimetres and their tenths.

If, for example, two grammes of the assay substance have been weighed out, the assay fluid measured at 200 cubic centimetres, and five cubic centimetres of it diluted to 8.2 cubic centimetres in order to obtain an equal intensity of color between the normal and assay fluid, then the percentage of copper, x, follows from this according to the following chain of ratios:—

x	100 per cent.
2	200 c. c. assay fluid.
5	8.2 c. c. diluted assay = normal solution.
5	.0025 grammes of copper in normal solution.

x = 8.2 per cent. of copper.

b. *The assay fluid is lighter than the normal solution.* In this case five cubic centimetres of the normal solution are diluted till their intensity is equal to that of the assay solution that has been measured at a definite volume, and for the comparison larger tubes of nine millimetres interior diameter are used.

If, for example, two grammes of the assay substance have been weighed out, 150 cubic centimetres of assay fluid obtained from it, and to get the same intensity of color, five cubic centimetres of the normal solution diluted to 8.4 cubic centi

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metres, the quantity of copper x amounts according to the following chain of ratios, to 2.205 per cent.

x	100 per cent.
2	150 c. c. assay solution.
8.4	5 c. c. normal solution.
5	.0025 grammes of copper.
$x = 16.8$	$37.5 = 2.205$ per cent.

This assay is adapted for all cupriferous substances, since nickel, cobalt, and manganese, which would influence the result unfavorably, can be removed without particular difficulty (page 89). It is also easy to be learned by those less practised in analytical operations, can be completed in a few hours, and is far less expensive than the dry assay. From two to one tenth per cent. of copper even can also be determined by it with accuracy.

Heine, however, prefers his method when a small percentage of copper is to be determined, since by it even one loth of copper in the centner = .03 per cent. can be determined, and there is less liability to error. While in slag assays with nine to eighteen loth of copper in the centner, by *Heine's* method, errors of half a loth are not to be avoided, variations of more than one loth occur by *von Hubert's* process. The latter works with a too deeply colored normal fluid, which corresponds to a solution of over fourteen loth of copper to one ounce of water, while *Heine* does not exceed four loth. The process is surer if the fluids are diluted and thicker layers of them compared, and thus the hue made artificially deeper, than if small quantities of stronger fluids are compared and the hue made artificially lighter by comparing them in thinner layers, or especially in tubes, where the light is dispersed and shade produced. The comparison in oblong glasses is therefore to be preferred to that in tubes.

By a comparison of *von Hubert's* assay with that of the

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Oberharz (page 75) it appears that, as *von Hubert's* experiments themselves have shown, both give equally accurate results for substances not too poor in copper (*i. e.* containing not less than .5 per cent.). The *Oberharz* assay allows a direct determination of the copper, requires less apparatus, is also very simple, and can be completed in a shorter time. Since different individuals are differently susceptible to colors, and the blue color of the ammonio-oxyd of copper, in consequence of causes yet unknown, sometimes inclines more or less to greenish and thereby renders observation difficult, therefore for the sake of greater certainty though not of greater accuracy, those assays should in general be preferred to the colorimetric methods, by which a determination of the copper is possible by weight, and this is the case with the Oberharz assay down to two per cent. With smaller percentages the colorimetric assay must be called to our aid. It is not yet settled that with higher percentages of copper the principle of colorimetry is a correct one, that is, that the intensity of the color is directly proportional to the quantity of the coloring agent.

Since ammoniacal solutions poor in copper often show a dash of greenish, *von Hubert* prepares a normal solution for such by dissolving one decigramme of copper and diluting to one litre of fluid.

3. *A. Müller's assay with the complementary colorimeter.*

Müller has sought to remove the uncertainties in the comparison of colors which arise in direct inspection, by a new colorimeter, which is based upon the neutralization of the color to be measured, by its complementary color. For cupriferous ammoniacal fluids a more or less reddish yellow is suitable, according to their character.

This process, for the detailed management of which reference must be made to the publications of Müller, consists

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essentially in determining in millimetres the height of the column of fluid of a dilute ammoniacal solution with a known percentage of copper, which, when the laterally falling light is cut off, with a complementarily colored glass plate placed over the fluid, will produce the neutralization point, *i.e.* white light. For every testing of an assay fluid instituted with the same glass plate, the percentage of coloring matter then follows in inverse proportion to the actual height of the column of fluid. If the volume of the assay fluid is also measured, which is directly done with great accuracy in the apparatus itself, all the data are obtained for the calculation of the amount of copper in the assay substance, after the necessary corrections, constant for each instrument, have been taken into consideration.

As the experiments of *Heine*, and also investigations made in the metallurgical laboratory at *Clausthal*, have demonstrated, large and small quantities of copper can be quickly determined with great accuracy by means of this colorimeter.

c. *Volumetric copper assays.*

Volumetric methods for the determination of copper have been proposed by *E. de Haen*, *Lieshing*, *C. Mohr*, *Pelouze*, *Streng*, and *Schwarz*. For docimastic purposes are to be recommended under certain circumstances the methods of *Pelouze* and *Schwarz*, as also the latter with the modification of *F. Mohr*.

1. *Pelouze's copper assay (precipitation analysis) with sulphid of sodium.*

This is based upon the fact that copper in its blue ammoniacal solution is precipitated by sulphid of sodium before most other metals (lead, tin, zinc, cadmium, iron, antimony, arsenic, etc.), and the completion of the reaction is indicated by the disappearance of the blue color. During the process, however, the copper solution must be heated to 65—85° C.,

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for only then does a permanent compound of 5 Cu S + CuO form.

After the ammoniacal solution obtained from one gramme of the assay substance has been heated in a beaker to 65—85°C., titrated solution of sulphid of sodium is added to it from a burette, until the blue color has disappeared. From the quantity of the solution of sulphid of sodium used, about thirty to thirty-two cubic centimetres of which must precipitate one gramme of copper, the quantity of copper in the assay can then be calculated.

Nickel and cobalt interfere somewhat with the reaction on account of their coloring properties.

For the preparation of the *sulphid of sodium, a caustic soda lye* is first produced. One part of purified crystallized carbonate of soda of commerce is dissolved in five parts of water, brought to boiling in a clean cast-iron kettle, and lime pulp added (with avoidance of all wooden spoons, etc.), at intervals of a few minutes, till a small quantity of the lye, after filtration, no longer effervesces with sulphuric acid. (The lime pulp is produced by pouring at once over the caustic lime in an earthen vessel sufficient water to convert it into a thin pulp.)

The solution is further boiled about a quarter of an hour, the kettle then removed from the fire, provided with a clean cover, and the lime allowed to settle in it for about six hours. The lye is then drawn off with a syphon into flasks, which are immediately closed with corks well sealed with wax. The residue is once more stirred up with water, allowed to boil awhile, then to settle, and drawn off. The lye is then evaporated in the cleaned kettle to a specific gravity of 1.16. After it has become cool in the covered kettle, it is drawn off into flasks which are closed and sealed like the others. Through the stopper pass two tubes air-tight, one a syphon tube provided at the bottom with a spring cock or clamp

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(Figs. 25–26), and one, an ordinary chlorid of calcium tube, into which a cotton wad is loosely shoved, and on this a mixture of sulphate of soda and caustic lime placed to absorb the intruding carbonic acid. Crystallized sulphate of soda and quick-lime are triturated together in about equal volumes, allowed to slake completely, and the mixture, which absorbs carbonic acid with great avidity, dried over an open fire. By opening the spring cock the fluid flows out.

Washed hydrosulphuric acid gas is conducted into the caustic soda lye till a sample of the fluid mixed with solution of sulphate of magnesia is no longer rendered turbid. The proper *solution of sulphid of sodium* is then obtained.

In order that no bubbles and no foam may be formed in pouring the titrated fluid into the burette, it is first poured into a small inclined funnel so that the fluid may run down the sides of the tube. The latter, which is placed perpendicular in a stand (Fig. 25), is filled above the zero point with fluid, the spring cock then quickly opened in order that all the air may be driven out, and the fluid allowed to sink so far that the lower edge of the concave arc, the meniscus formed by its surface, is exactly even with the zero mark. After the assay, the lowest point of the arc is again taken as the guide in the reading.

Instead of the spring cock burette the burette of *Gay Lussac*, or a modification of the same by Mohr (Fig. 27), or any other convenient form of burette may be used.

This assay, to be recommended for its quickness, is only adapted for more or less pure copper and its alloys; with more complex substances, ores, metallurgical products, etc., the end of the reaction does not distinctly appear, since brownish or greenish shades of color are produced, which conceal the blue. Another drawback is the gradual changing of the solution of sulphid of sodium by access of air, so that it must be frequently titrated.

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2. *Schwarz's method with the modification of F. Mohr.*

.634 grammes of the assay substance are dissolved in water or acid, the solution placed in a flask, the excess of acid neutralized with carbonate of soda, a small quantity of neutral tartrate of potassa and caustic potassa or soda added till all is dissolved to a deep blue fluid. If this does not take place at once, more tartrate of potassa is added. The solution is warmed to 40–50° R., and pure starch- or honey-sugar, or pure white honey added, with frequent shaking, whereby the oxyd of copper is gradually reduced, and finally a fire-red precipitate of suboxyd of copper produced, so that the fluid assumes a yellowish color. With too strong boiling the precipitate becomes brownish red. The diluted fluid is filtered, the precipitate well washed with hot water, and together with the filter put into a wide-necked flask, and a suitable quantity of chlorid of sodium, and then hydrochloric acid added, whereupon the suboxyd of copper dissolves to colorless subchlorid of copper, forming an easily soluble double salt with the chlorid of sodium. Without removing the filter, titrated solution of permanganate of potassa is then added to the solution from a *Gay Lussac* burette, with constant stirring until its rose-color, which is destroyed by the oxydation of the suboxyd of copper, again appears. The permanganate of potassa solution is so titrated that 100 cubic centimetres of it correspond to .56 gramme of iron. The cubic centimetres used then give the copper in per cents.

The calculation depends upon the fact that one atom of suboxyd of copper, Cu_2O, takes one atom of oxygen from the permanganate of potassa to form oxyd of copper, and two atoms of protoxyd of iron, which contain two atoms of iron, also take one atom of oxygen to form sesquioxyd of iron; hence one atom of iron corresponds to one atom of copper, or twenty-eight of iron to 31.7 of copper, so that from the per-

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centage of iron which the titrated solution of permanganate of potassa gives, the percentage of copper may be calculated.

This method gives accurate results, and is only on account of the filtering somewhat minute in detail.

D. *Other copper assays.*

Copper assays have also been proposed by *Levol*, and *Byer* and *Robert*, as well as *Rivot*.

1. *Levol* treats a solution of ammonio-oxyd of copper, with exclusion of air, with a weighed strip of copper, by which the oxyd of copper is reduced to sub-oxyd. From the loss which the strip of copper suffers, the quantity of copper in the solution can be calculated. This assay is indeed accurate, if no other substances are present which oxydize copper, but it requires several days' time, and the copper is determined by a difference, which is always more uncertain than a direct determination.

A similar assay, in which, however, instead of an ammoniacal solution, a hydrochloric acid solution is used, has been given by *Runge*.

2. *Robert* and *Byer* precipitate the copper from its solution, by a simple galvanic apparatus, on a weighed plate of copper, whose increase in weight then gives the quantity of copper in the assay. The operation lasts ten to twelve hours, and no other similarly precipitable metals should be present.

3. *Rivot* precipitates the *suboxyd* of copper from its solution as sulphocyanid of copper $Cu_2 Cy_2 S$, and from the weight of this salt calculates the amount of copper directly, or after it has been converted into Cu_2S by igniting with sulphur in a covered porcelain crucible at a red heat.

This method is indeed accurate, and generally practicable, but it requires a complete acquaintance with the analytical operations and the observance of a mass of small precautions, so that it does not differ from an analytical process.

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Sulphid of copper obtained by precipitating with hydrosulphuric acid passes by ignition with sulphur after drying into Cu_2S, from which the copper may be calculated.

II.—ASSAYS FOR SUBSTANCES POOR IN COPPER.

Colorimetric copper assay.

For substances poor in copper (slags, refined lead, crude lead, etc.) *Heine's* method (page 81) is exactly suitable, since smaller quantities of copper (.03 per cent.) can be determined by it with greater accuracy than by the colorimetric methods of *Jacquelain* and *von Hubert* (.1 per cent.). By means of *Müller's* complementary colorimeter, in five cubic centimetres of solution, .05 per cent. of copper in the assay can be determined; but *Heine's* process requires less complex and costly apparatus.

"*Copper slate*" must, before the treatment with acids, be ignited.

ADDITIONAL REMARKS UPON THE COPPER ASSAY.

Charging of the copper assay at Schemnitz.

To one centner of well-roasted assay powder, three centner of black flux, ten to twelve pounds of borax, and a chlorid of sodium covering.

Fleitmann's copper assay.

The following courses are pursued, according as nitric acid is used or not for the solution of the cupriferous substance.

1. If the solution is *free from nitric acid* and from troublesome metals, such as antimony and arsenic, the copper is precipitated with zinc, the excess of zinc removed by digesting with dilute sulphuric acid, and the precipitate well washed

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and dissolved in an acid solution of sesquichlorid of iron. The solution takes place rapidly, and yields the double equivalent of protoxyd of iron, which is determined with titrated solution of permanganate of potassa in the usual manner (page 98). The solution in chlorid of iron and the determination with permanganate of potassa, takes hardly so much time as the drying and weighing of the spongy copper.

2. *In the presence of nitric acid* the oxyds of iron, lead, bismuth, etc., are precipitated by ammonia, the fluid filtered, and the copper precipitated from the ammoniacal solution with finely rasped or scraped zinc. The precipitation proceeds rapidly at a moderate heat, and its completion may be known, in the absence of nickel, by the disappearance of the blue color. The copper is then treated as above.

If *arsenic* is present it is converted into arsenic acid in the solution by the addition of nitric acid, chlorate of potassa, etc., then mixed with ammonia in excess, arsenate of ammonia and magnesia precipitated by sulphate of magnesia, the mass filtered, and the copper thrown down from the filtrate as above.

Heine's colorimetric copper assay.

In order to find the very small quantities of copper that injure *lead*, that is to be used in the manufacture of white lead (.01 per cent. and less), as high as thirty assay centner of the substance must be dissolved in nitric acid, the solution evaporated to dryness with sulphuric acid, the dry mass extracted with water containing sulphuric acid, and then ammonia added.

Volumetric method with cyanid of potassium.

According to *Mohr*, the cupriferous compound is brought into ammonio-oxyd solution, and a titrated solution of cyanid of potassium added, until the blue color disappears, without

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the formation of a precipitate. The cyanid of potassium solution is titrated by means of metallic copper, so that one cubic centimetre of it corresponds to .01 gramme of copper.

This method is far preferable to that of *Pelouze*.

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ASSAY OF SILVER.

CLASSIFICATION OF SILVER ASSAY.

THE determination of the quantity of silver in ores, metallurgical products, etc., may be accomplished in the dry or in the wet way.

The *assays of silver in the dry way* belong to the oldest and most accurate processes which the art of assaying possesses. For their correct execution, attention and practice are especially required, as also a proper choice of the method of examination for the precise case in hand. All assays in the dry way amount in the end to this: that the silver contained in the assay sample is obtained combined with lead, and then the lead removed from the argentiferous button by a process of oxydation (*cupellation*) which is performed upon a porous vessel (*a cupel*). The latter absorbs the oxyd of lead formed together with the foreign oxyds, while the silver remains behind.

This process is subject to manifold causes of error, among which the main one is the loss which takes place through volatilization of the silver, and through its oxydability.

Silver is in itself somewhat volatile, and when it comes in the shape of vapor into contact with the air it gives a red smoke (characteristic deportment before the blowpipe). Silver is also often disposed to volatilization by certain other substances which become volatile at a high temperature, especially by the compounds of arsenic, antimony, zinc, and lead, which often occur with silver, as well as by an admixture of

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chlorid of sodium, as the researches of *Plattner*, *Malaguti* and *Durocher*, *Klasek* and others have proved.

Silver is in itself difficultly oxydizable, but becomes oxydized by the presence of excess of oxyd of lead, remains with the latter in the state of oxyd, and passes together with it into the cupel, and hence arises the loss of silver by the *absorption of the cupel.* This loss increases with the amount of silver in the assay sample, but on the other hand, with small quantities of silver, as *Malaguti's* and *Durocher's* experiments have shown, it scarcely allows itself to be determined. In poor argentiferous substances, and especially in commercial ore assays, this loss is not brought into consideration, on account of the loss of silver in working silver ores in the large way, as well as on account of the unavoidable absorption by the cupel in assaying the refined silver produced; on the other hand, it is taken into consideration in rich silver alloys, according to tables, the formation of which is based upon the results of accurate investigations (see the fine silver assay).

According to *Plattner*, the absorption by the cupel, with a content of one per cent. of silver, is indeed not at all perceptible by means of the balance; but becomes so, when the globule of silver obtained is large; and reckoned according to its *percentage of the silver present*, it increases again, the smaller the globule of silver is.

According to *Bodemann* the absorption by the cupel, in ores with a few loth of silver in the centner, amounts to two to five per cent. of the silver contents. At the St. *Andreasberg* silver refinery, the absorption by the cupel, according to *Seidensticker*, reckoned according to its percentage of the silver button obtained from the ore, is taken at

4	per	cent.	with	$1\frac{1}{4}$—4	loth of silver in the centner of ore.
3	"	"	"	$4\frac{1}{4}$—8	
2	"	"	"	$8\frac{1}{4}$—16	
1	"	"	"	$16\frac{1}{4}$—24	
$\frac{3}{4}$	"	"	"	$24\frac{1}{4}$—480	

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The quantity of lead and the temperature used in the cupellation, as well as the greater or less porosity of the cupel, exercise an important influence upon the amount of the absorption.

If the litharge absorbed by the cupel is reduced by a lead assay, and the lead obtained from several such assays collected, and without the addition of assay lead scorified and cupelled, the amount of the absorption by the cupel can be determined. A loss of silver by the absorption of the cupel again takes place indeed in this cupellation, but the amount of it, in comparison with the whole amount of silver to be found in the alloy, is considered too small to deserve any further notice.

In the cupelling in the large way, silver is indeed also absorbed along with the litharge into the substance of the hearth; but by breaking up the hearth and mixing it with the next smelting charge, the silver contained in it is for the most part recovered, so that the product is greater than it should be according to the assay, in which the absorption by the cupel is not taken into consideration. A compensation for other losses, therefore, accrues to the smelting-house through the absorption by the cupel.

Although the dry silver assay, according to the above, gives the amount of silver too small by a variable quantity, it nevertheless allows of as high a degree of accuracy as almost any other metal assay in the dry way, while by it, as *Malaguti's* and *Durocher's* experiments have proved among other things, the presence of the smallest quantities of silver, which elude all weighing and measuring ($\frac{1}{100}$ milligramme), can be distinctly shown. The higher the percentage of silver in the ore, the more uncertain becomes the assay.

The wet silver assay, by which is generally understood the determination of the silver, according to the directions of *Gay Lussac*, by means of a titrated solution of chlorid of

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sodium, with smaller percentages of silver, allows of great errors or yields no silver at all, but permits a more accurate determination than the dry way in substances rich in silver (alloys), which can be easily brought into solution. This method is therefore generally used only in assaying bullion, etc., in mints, for the exact determination of the percentage in silver alloyed with copper.

As already stated, this assay is based upon the precipitation of the silver previously brought into solution, as chlorid of silver by a titrated solution of common salt. Since chlorid of silver is somewhat soluble in solution of chlorid of sodium (one part in sixty parts), small quantities of silver, *e. g.* $\frac{1}{2000}$, are not precipitated at all by the latter. Indeed, a portion of chlorid of silver dissolves also with substances richer in silver, in the chlorid of sodium, but the loss thus arising becomes vanishingly small. It varies essentially as the whole volume of the solution, and for equal volumes it remains almost constant in different silver solutions, from which it appears that the more silver is contained in the assay sample, the more accurately is it determined.

The silver assays in use may be classed as follows:

A. *Assays in the Dry Way.*

I.—ORES AND METALLURGICAL PRODUCTS THAT ARE NOT ALLOYS.

A. *Scorification assay for substances rich or poor in silver* (native silver; antimonial silver, Ag_3 Sb and Ag_4 Sb, with respectively 84 and 77 per cent. Ag; telluric silver Ag Te, with 61 per cent. Ag; silver glance Ag S, with 87 per cent. Ag; brittle silver ore, 6 Ag S, Sb S_3, with 70.4 per cent. Ag; light red silver ore, 3 Ag S, As S_3, with 65.4 per cent. Ag; dark red silver ore 3 Ag S, Sb S_3 with 59 per cent. Ag; light and dark fahlerz with respectively 5.7 and 18–31.8 per cent. Ag; argentiferous sulphid of copper Cu_2 S, Ag S, with 53 per cent. Ag; polybasite, 9 [Cu S, Ag S] + [Sb S, As S_3], with

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72 to 94 per cent. Ag; argentiferous lead, copper, zinc, and arsenic ores, matte, speiss, slags, etc.).

B. *Fusion assay for ores rich in lead but poor in silver, e. g.* the Oberharz galena slick.

C. *Fusion assay for poor, pyritiferous silver ores, e. g.* pyrites, pyrrhotine, etc.

D. *Fusion assay for earthy substances poor in silver, e. g.* tailings, slags, etc.

II.—ALLOYS.

A. *Alloys poor in silver* (refined copper, black copper, brass, etc.).

B. *Rich silver alloys*, particularly of silver with copper (mint assay, fine silver assay).

B. *Assays in the wet way.*

A. *Volumetric assay of Gay Lussac* for rich alloys of silver with copper (mint assay).

B. *Other assays in the wet way.*

Section First.

A. SILVER ASSAYING IN THE DRY WAY.

I.—ASSAYS FOR ORES AND METALLURGICAL PRODUCTS, THAT ARE NOT ALLOYS.

A. *Scorification assay for substances poor or rich in silver.*

This assay falls naturally into two periods, namely, first into the fusing of the assay substance with metallic lead, in which the silver is taken up by the lead, and the superfluous lead and foreign ingredients slagged off; and secondly, into the cupellation of the argentiferous lead, or the separation of the silver from the lead.

A centner of the ore, etc., is mixed with eight centner of granulated lead (assay lead) in such a way that about half of the lead is *mixed* with the ore in a scorifier (Fig. 12), and

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this covered over uniformly with the remainder of the lead. Fluxes are also required, according to the nature of the ingredients present, and, indeed, according to whether the latter are of metallic (zinc blende, pyrites, etc.) or earthy nature. The earthy substances separate again into basic (calc spar, dolomite, barytes, fluor spar, etc.), and acid (quartz, silicates, clay, aluminates, etc.). Silver ores which contain much earthy gang are called dry ores (Dürrerze), and if sulphids are present at the same time, they are designated as pyritiferous, blendy, etc. The fluxes consist principally of borax, quartz, or glass. Basic and very difficultly fusible ores require the most *borax* (up to 50 per cent.), which takes up the bases, and renders the compounds formed more fusible. Acid ores need only a small addition of borax, or none at all, though a small quantity of it (perhaps ten per cent.), as a means of promoting fusion, does no harm. The borax is stirred up together with the ore, or is placed on top as a covering. Too much borax works disadvantageously, especially with substances rich in sulphur and arsenic, since then the covering of slag becomes too great from the beginning, and not sufficient oxyd of lead can form to decompose the metallic sulphids; in consequence of which, oxysulphurets containing silver remain in the slag. If a large addition of borax is needed, *e.g.* in the presence of much tin, zinc, lime, etc., a part of it must be added afterwards, before the final strong heat is applied, especially also in the presence of a large quantity of iron.

With ores containing extremely little or no silica, either free or combined, an addition of a few assay pounds of *glass* or *quartz* is advisable, since by this a too rapid eating through of the scorifier by the oxyd of lead formed is counteracted. These may be added either at the same time with the borax or subsequently. Also the scorifier may be coated over with a thin layer of quartz or glass. With good scorifiers, however, such an addition is unnecessary.

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The *quantity of lead to be used* depends upon whether the ores contain little or much of substances, particularly sulphids, whose constituents are disunited with difficulty by air or litharge. In many cases the ratio of one centner of ore to eight centner of lead suffices; if *zinc blende* or *pyrites* is present in large quantity, this ratio rises to twelve to sixteen-fold; with much *copper* and *tin* compounds, to twenty to thirty-fold; with *nickel* and *cobalt* compounds, yet somewhat higher, unless these are smelted beforehand with ten parts litharge and two parts of saltpetre. *Nickel speiss* must be scorified two or three times with sixteen times its weight of lead. In general, also, the more silica, etc., is present, and the longer the desulphurizing requires, the more lead is to be used. Too great an addition of lead prolongs the operation, and in consequence of this, increases the loss of silver. At the *Freiberg* refinery the ores are generally scorified with ten to fifteen parts; at the *Hartz* refineries with eight parts of granulated lead. The quantity of silver in the lead, if it is vanishingly small, is not taken into consideration (as at *Freiberg*),—or the same quantity of lead that was used in the assay is scorified and cupelled alone, and the globule obtained is laid with the weights, in weighing the assay globule (as in the *Hartz*). The *Freiberg* assay lead contains from .0001 to .0009 of a pound of silver in the centner; that of the *Hartz* one-eighth loth. With rich silver ores, *e. g.* red silver ore, antimonial silver, etc., only twenty-five to fifty assay pounds are generally weighed out with sixteen to thirty-two parts of lead, and the necessary addition of borax given.

The charged scorifiers are placed in the bright red-hot muffle, and this, in order to bring the lead quickly into fusion, is closed by laying glowing coals before it. As soon as the lead is in thin fusion, it will be seen that the ore, owing to its lighter specific gravity, has risen to the surface of the metallic bath and here undergoes roasting. From the appearance or

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smell of the vapors rising from the assay, we can often judge with certainty as to the nature of the substances passing off in the roasting. Sulphur gives light gray, zinc thick white, arsenic grayish white, antimony bluish vapors.

To subject the ore to be examined to a special roasting before the scorifying, is not only unnecessary, but even entirely injudicious, because by a separate roasting a slight loss at all events cannot be entirely prevented.

After fifteen to twenty minutes the surface of the assay has generally become more or less smooth, and a fluid slag has formed which completely surrounds the periphery of the molten, reddish-white glowing metal, from which thick fumes of lead are rising. The time required for this fusing differs with the character of the assay; with very difficultly fusible assays as much as thirty to thirty-five minutes may be necessary, but generally the above time is sufficient.

The muffle is now almost entirely opened, the draft closed, and with full access of air, a slagging off of the lead and other scorifiable constituents goes on (perhaps ten to fifteen minutes) until by further oxydation of the lead the slag has so far accumulated that it completely or almost completely covers over the metal. Then finally a short strong heat (of about five minutes) is again given, in order to render the slag completely fluid, and to separate any mechanically inclosed lead.

It is advantageous in general to carry the scorification as far as possible, since experience has shown that in this operation less silver is lost than in the cupellation following, if the lead button is larger. Still by continuing the scorification too long, the oxyd of lead is apt to destroy the scorifier. The scorification should not last over an hour at most, generally half an hour suffices.

The assays are now removed from the furnace, and alloy and slag are poured out into the depressions of the previously warmed pouring-plate (assay plate) which have been pre-

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viously rubbed with rouge or chalk, so that the assays may afterwards easily and completely loosen from them without sticking.

If the pouring-plate is not warmed in cold weather, a brittle lead is often obtained that is difficult to hammer. Copper pouring-plates rubbed with rouge are to be preferred to iron ones, since on account of the sudden cooling of the assay that takes place in the latter, particles of lead often remain in the slag.

For the removing of the scorifiers from the furnace, and for pouring them, it is safest to use the scorifier tongs (Fig. 21). In the pouring, not the least particle of metal should remain behind in the scorifier. Assays with a stiff slag have either not had a proper quantity of flux (borax, and litharge arising from the oxydation of the lead), or the heat has not been sufficiently prolonged. With such there is danger that little separate granules of lead will remain suspended in the glutinous mass of slag, and thus the amount of silver be found too small.

The lead alloy obtained in the scorifying must be quite malleable. If it is brittle this indicates that the roasting was imperfect, or that the scorification has not continued long enough, or that too little lead was used for the assay. Assays, the lead alloy of which, in the succeeding hammering, exfoliates mechanically-inclosed litharge or slags, have, at least towards the end of the operation, not been kept hot enough.

After the cooling, the argentiferous lead button obtained, which must have collected into a single regulus, and must separate easily from the slag, is so hammered on the anvil that it can be easily and firmly seized with the tongs (Fig. 19 or 20) and placed on the cupel, without injuring the latter by projecting corners and edges.

Instead of pouring out the assays, when the scorification is finished, into the assay plate, they may also, and indeed with-

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out prejudice to their accuracy, be simply taken from the furnace, and, before the breaking up and freeing from slag, allowed to cool quietly in the scorifiers. Only the cooling then proceeds very slowly and consumes unnecessarily more time.

The chemical reactions in the scorification or slagging process depend partly on the roasting of the ore that takes place during the smelting, partly upon the peculiar power of the oxyd of lead produced to form a slag with all earths and oxyds of the base metals, and thus, if present in sufficient quantity, to act as a universal flux; and besides, also very essentially upon the influence that litharge exercises upon metallic sulphids, and which commences actively even at a moderate red heat.

The mutual decomposition of litharge and metallic sulphids has been most completely investigated by *Berthier*, who has found that if litharge is allowed to work in sufficient quantity upon metallic sulphids, with exclusion of the atmospheric air, the sulphids are completely decomposed. In general all the sulphur escapes as sulphurous acid gas, and the metal remains behind either alloyed with the lead proceeding from the reduction of the litharge, or else as oxyd, combined with the portion of litharge not reduced. The quantity of litharge necessary for the complete decomposition of a metallic sulphid is considerable, and is not the same for the sulphids of the different metals. If less is used than is required, only a part of the metallic sulphid is decomposed and a corresponding quantity of oxyd of lead reduced. The remainder of the oxyd of lead, and the metallic sulphid, together with the metallic oxyd that may be formed from the latter, unite into a compound which belongs to the oxysulphurets, and is in general very fusible. *Sulphid of copper* forms an exception to the last statement, since it forms no oxysulphuret by fusing together with litharge. Generally the union of the litharge

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with the metallic sulphid is very intimate; by a greater addition of litharge, however, these oxysulphurets are completely decomposed. Many oxyds also, by combining with the oxyd of lead, considerably impair its decomposing effect upon the metallic sulphids. The sulphids of the metals of the alkalies and alkaline earths evolve no sulphurous acid with litharge, but all the sulphur is changed to sulphuric acid. In relation to the other more frequently occurring metallic sulphids experiments give the following:—

Sulphid of copper is completely and easily decomposed by litharge, with evolution of sulphurous acid and simultaneous formation of suboxyd of copper and metallic lead, but to this end twenty parts by weight of litharge are required to one part of sulphid of copper. Oxyd of lead which is already combined with a considerable quantity of suboxyd of copper, works no further upon sulphid of copper. *Sulphid of mercury*, cinnabar, requires about ten to twelve parts by weight of litharge for its complete decomposition, during which metallic mercury volatilizes. *Sulphid of bismuth* requires for its complete decomposition twenty parts by weight of litharge. The whole of the bismuth then alloys with the lead, and does not combine as oxyd with the litharge. *Sulphid of molybdenum* requires forty to fifty parts of litharge by weight in order to be entirely decomposed. No alloy of molybdenum and lead is formed in the process, but all the molybdenum is oxydized. *Sulphid of manganese* needs for its desulphurization thirty parts by weight of litharge. The manganese is only oxydized to the protoxyd, but if the air has access at the same time, it oxydizes higher. *Protosulphid of iron* is decomposed by thirty parts by weight of litharge, and the iron, provided that no access of air is allowed, changed to protoxyd. *Iron pyrites*, on the other hand, requires up to about fifty parts by weight of litharge, if it is to be entirely decomposed by this alone. *Copper pyrites* requires at least thirty parts by weight

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of litharge for its decomposition. With *sulphid of zinc* (blende) twenty-five parts by weight of litharge suffice for decomposition and scorification, in which all the zinc is oxydized. *Sulphid of tin*, mosaic gold (aurum musivum), requires twenty-five to thirty parts by weight of litharge; no alloy of lead with tin forms; the latter oxydizes. *Sulphid of antimony* requires at least twenty-five times its weight of litharge, and the antimony goes as oxyd into the slag. With a small addition of litharge it is very apt to form oxysulphurets. *Sulphid of arsenic*, orpiment, forms compounds with oxyd of lead that are uncommonly fusible, and can be completely desulphurized only by a great excess of litharge. To one part, fifty to sixty parts by weight of litharge at least must be used. The lead then separated contains no arsenic. The latter is also oxydized by the litharge. *Sulphid of lead.* Galena and litharge work upon each other at a red heat in such a way that they mutually decompose one another, without forming any oxysulphuret in the process. If two equivalents (5578) of litharge are used to one equivalent (2991) of galena, or 1865 litharge to 1000 galena, only pure metallic lead is obtained. If the litharge predominates, a part of it is not reduced, and this then covers over the lead. If, on the contrary, galena is in excess, a subsulphid of lead is formed, which with slow cooling deposits itself on the separated metallic lead. But if the litharge is combined with a certain quantity of any other oxyd or metallic sulphid, it loses its oxydizing power over the galena, and can then combine with it, as with other metallic sulphids, without a mutual decomposition taking place. A new addition of litharge, however, destroys this oxysulphuret also. *Arsenical nickel* needs a large quantity of litharge for its full decomposition.

It has already been stated that in these experiments the excess of air was prevented. They were undertaken in a temperature which a muffle furnace easily produces.

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We observe now that, in the scorification, if the assay sample, as is the case with most ores, contains metallic sulphids, the roasting of the ore commences indeed with the melting but that the decomposition first advances more rapidly when a part of the lead has oxydized, and thus the working of the oxyd of lead comes also into play. The slagging off of the earths and oxyds contained in the ore first begins after a larger quantity of litharge has formed.

The stronger the affinity of the foreign metals for oxygen, the more apt are they to accumulate at the beginning of the process in the state of oxyds, and they may cause a *freezing* of the assay, *e. g.* iron, tin, zinc, etc.

The desilverizing of the assay is accomplished in part by the lead, which, in the fusion of the sulphids, extracts their silver with the formation of sulphid of lead, but principally by the working of litharge on the sulphid of silver. The white parts often separating out over the slag in the pouring of the scorification assay, are either undecomposed quartz or sulphate of soda, formed from the sulphur of the ore and the soda of the borax.

For the whole process of scorification one half to one hour is needed, and the result of a rightly conducted assay is that the assay substance is now completely decomposed by the roasting and the working of the litharge, and thus no oxysulphuret, which might yet retain some silver, is any longer to be found in the slag; that the earths and oxyds present, aided by the addition of borax, have united with the litharge to a perfect and easily fusible slag; and that the silver, in whatever combination it may have been held in the assay substance, has alloyed with the remaining lead, and completely collected itself in it.

If a roasting did not take place simultaneously with the scorification, it would often be necessary to largely increase the addition of lead in order to obtain the quantity of litharge,

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which, according to the results of experiments given, is required for the decomposition of the argentiferous metallic sulphids.

With the nature of the foreign ingredients, the scorification suffers various modifications, especially with respect to the temperature to be employed, and the duration of the separate periods. In *Freiberg* the following chargings are in use:

Argentiferous galena with sixty to eighty per cent. of lead is mixed with six centner of lead and 0–15 per cent. of borax. If pyritiferous or blendy minerals are present, the lead is increased up to eleven centner, and the borax to twenty to thirty per cent.

Ordinary "Dürrerze" containing silver glance, ruby silver, iron pyrites, zinc blende, spathic iron, calc spar, etc., require, on account of the large amount of sulphids present, to one centner of ore, twelve to fifteen centner of assay lead, and, at most, fifteen per cent of borax. In case of necessity, more borax is added afterwards. The charge is quickly fused, and the scorification long continued, and finally a strong heat is applied. *Basic "Dürrerze"* require eight centner of lead, and twenty-five to fifty per cent. of borax, which is partly added afterwards; *acid "Dürrerze,"* eight centner of lead and 0–20 per cent. of borax; *pyritiferous "Dürrerze,"* twelve to fourteen centner of lead, and ten to fifteen per cent. or more of borax.

Cupriferous ores require the addition of so much lead (ten to twenty parts), that the lead-button obtained for cupellation shall contain at least sixteen to seventeen times more lead than copper, as the latter is not completely slagged off in the scorification. Fahlerze, for example, are scorified with twelve centner of lead and fifteen per cent. of borax.

Zinciferous ores require ten to sixteen centner of lead and fifteen to twenty-five per cent. of borax, and need particular attention in the process. The zinc must be volatilized and as little as possible of the zinc oxyd formed, since this dis-

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solves with difficulty and gives a very difficultly fusible slag. In order that as little roasting as possible may take place, the assay is fused at a high temperature. If the slag becomes too stiff, a glowing coal is laid upon the assay, whereby the zinc is reduced and volatilized, the metallic bath again becomes smooth, and the proper oxydation of the lead first begins. According to *Ziervogel*, zinciferous ores, scorified in the usual way, give always a fluctuating percentage of silver. They must first be smelted to a matte, which is then scorified. Also several centner of zinciferous ore may be treated with aqua regia, and the residue scorified, *e. g.* pure blende.

Arsenical ores require a high temperature in the scorifying, in order to give a perfectly fluid slag. A rim of stiffened slag containing silver is very apt to form. This can sometimes be removed if a glowing coal is held over it, or borax is added. With poor arsenical ores, as high as sixteen parts of lead, and fifty per cent. and more of borax, are taken to one part of the ore.

Rich arsenical and antimonial silver ores can, in general, only with difficulty be assayed by the scorification method, and it is often better to use for such the *Andreasberg* method, page 126, or the *English* one, page 129. 3.

Nickeliferous and cobaltic silver ores, speiss, etc., are scorified at a high temperature, with as high as twenty parts of lead, and borax is added later in the process. As the scorifiers do not hold twenty centner of lead, generally fifty pounds only of the assay substance are taken.

Ores containing tin are scorified several times with much (twenty to thirty parts) lead and borax, in order that the assay may not "freeze" in the cupellation by the formation of uncombined oxyd of tin.

Raw matte requires ten to twelve centner of lead, and, if zinc is present, even more, at first without borax, afterwards with the addition of as high as thirty per cent.

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Lead matte is scorified with nine to twenty centner of lead, at first with little, afterwards with twelve to twenty-five per cent. of borax; if nickel and cobalt are present, eleven to fourteen centner of lead are taken.

Copper matte with twenty to thirty per cent. of copper requires twelve to fifteen centner of lead. *Furnace deposits* like zinciferous "Dürrerze."

Lead speiss and *cobalt speiss:* one-half centner is scorified with ten to twenty parts of lead, and each two of the buttons thus obtained again scorified together.

Residues from the amalgamation of black copper and the silver extraction process, are generally treated without borax, one-half centner of residue with eight to ten centner of lead. *Amalgamation residues* from "Dürrerze" are treated like "Dürrerze." Two assays, of one centner each, are scorified, and the two resulting buttons united and cupelled together.

Earthy substances (*slime*, *dross*, *slags*, etc.). A number of assays (as high as thirty-two) are scorified like "Dürrerze," the resulting buttons of lead united, and again scorified to a single button, which is cupelled; or two centner of the finely pulverized substance, *e. g.* fusible slags, are scorified with eight to twelve centner of granulated lead. The silver contents of the latter must always be deducted.

Old hearths are scorified with eight parts of lead, and borax added as may be needed.

Dross, *argentiferous* and *auriferous waste*, *sweep*, etc., are pounded fine, calcined, one civil pound dried, the percentage of moisture determined, the residue rubbed fine and passed through a sieve which catches the granules of silver; the weight of the silver grains and of the dross determined, and the percentage of silver in each determined separately. The dross is mixed like "Dürrerze" with eight to nine centner of lead and a corresponding quantity of borax.

With *antimony ores* twenty-five pounds are scorified with

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four hundred pounds (four centner) of lead, and as high as fifty pounds of borax.

With *antimonial silver* not more than twenty-five pounds are scorified with thirty-two parts (eight centner) of lead, and as high as seventy-five pounds of borax. The more ore is taken for the assay the greater are the differences in the results.

When native silver, silver glance, red silver ore, and other rich silver ores which are not to be assayed in the ordinary way, are brought to the *Freiberg* smelting-works, the ores are either cupelled without preliminary examination, or if their whole quantity only amounts to a few pounds, they are worked up in crucibles or on assay vessels, and the payment is calculated without further examination, according to the quantity of metal thus obtained.

Markus examined matte (from the Hungarian so-called Reichverbleiungsprocess) with one mark twelve loth of silver in the centner, in the raw and roasted states, by means of the scorification assay, and the fusion assay with litharge (400 pounds), saltpetre (twenty-five pounds), metallic iron (twenty pounds), and the usual reducing and solvent agents. The highest percentage of silver was obtained by scorifying the raw matte.

Now follows the second operation of the silver assay, the *cupellation* of the argentiferous lead obtained from the scorification. This process of driving off the lead, etc.—which depends upon the fact that the molten red-hot alloy of lead and silver is so resolved by the atmospheric oxygen that all the lead is changed to oxyd (litharge), and the metallic silver remains behind, if the removal of the fused oxyd of lead combined with the foreign oxyds is provided for—belongs to the oldest of metallurgical operations, and is at the same time among the most perfect processes known to the assayer. As it is not of importance to the assayer, as it is to the smelter, to obtain and save both the silver and the oxyd of lead, and he

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has only the former in view, he employs in this process the cupel (Fig. 9). The cupels must, immediately before placing the lead alloy upon them, be so long and completely glowed out, or heated through in the highest heat of the muffle of the assay furnace, that they no longer retain any trace of moisture. If this is neglected, the aqueous vapor escaping through the molten lead will surely cause a sputtering. Moreover, the cupels must also have reached a perfectly bright-red heat before being charged, because it is necessary that the lead should quickly fuse and begin to be driven off. By too slow a fusion, little particles of lead are liable to remain hanging to the upper rim of the cupel, and thus their silver be lost for the assay. The size of the cupels must be in proportion to the quantity of lead to be driven off. In general it is better to take the cupels rather too large than too small. It may, perhaps, be counted upon that the cupels can absorb about twice their weight of lead; but this is to be taken as the maximum. In general practice not more than their own weight is willingly placed upon them. More cupels should never be worked with at once than can be heated with perfect uniformity in the middle part of the muffle. The front cupels are charged first, and then the remaining ones without any delay. The furnace must be so hot that its temperature, either not at all, or only for an exceedingly short time, requires to be again increased in order to bring all the assays to driving. As soon as they *drive*, that is, as soon as a movement can be distinguished on the bright clear surface of the red-hot melted alloy, the draft of the furnace is closed and the temperature lowered, while only a small coal is left lying before the mouth of the muffle. The assayer then sees upon the convex surface of the metal, and indeed the more distinctly the richer grows the alloy, little points and scales (litharge) which have less lustre than the rest of the surface, and withdraw towards the sides of the cupel.

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The movement of the driving mass from within outwards comes from the fact that the superficially cooled portions sink towards the bottom and give place to the rising warmer ones. From the convex surface of the metallic bath the beads of litharge fall to the margin.

It is a rule never to be neglected, that the assays must be "driven" at as low a temperature as possible, since reiterated experience shows that the less silver is carried along by the litharge into the cupel, the lower the heat in which the litharge is generated.

It is nevertheless just as great an error as the giving of too high a heat, to so far lower the temperature that the lead ceases to "drive." This is called a *freezing* or *drowning* of the assay. Such assays can indeed be again brought to "driving" by a higher heat, but in general their results then become erroneous.

The ascending lead-fumes and the glowing of the cupel give an admonition for the correct management of the temperature. If the former rise, slowly winding, to about the middle of the muffle, and if a ring of small indistinct crystals of oxyd of lead forms on the sides of the reddish-brown glowing cupel, the temperature is right. If the lead-fumes disappear immediately over the cupel, if the latter glows bright-red, and no crystals of oxyd form, it is too hot. If the lead-fumes rise to the arch of the muffle, and the sides of the cupel appear dark-brown, it is too cold, and the assay easily "freezes." In order to keep the temperature in the front and rear of the muffle as uniform as possible, empty scorifiers are placed in several ranks over each other in the back part, or the back assays are cooled by means of a cooling-iron (Fig. 22) more than the front ones. The crystals of litharge are, according to *Hausmann*, very thin, elastic-flexible, strongly-brilliant, translucent, six-sided tables, which in loose aggregation sometimes form beautiful groupings.

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Towards the end of the process, the temperature must be again raised, because the metallic button becomes more difficultly fusible as the proportion of silver in it increases, and moreover, the last part of the lead is entirely separated as litharge, and completely absorbed by the cupel, only at a somewhat increased temperature. The heat should not be increased too soon, and should only be raised gradually, but never so high that the rim of crystals of oxyd again fuses.

> "Cool to drive and hotter 'blick'
> Is of assaying the master trick,"

is very old, and contains for the process in hand a very important truth.

The richer is the ore to be examined, and the greater accordingly is the resulting button of silver, so much the more, after the *blicking* (or brightening) of the assay—that is, after the last reticulated remnant of litharge and the rainbow-play of colors have disappeared from the surface of the metal—must the assayer guard against a too rapid cooling and solidifying of the assay, since a rapid cooling produces a tumultuous blossoming out of the silver—the so-called *sprouting* or *spitting*. This sprouting is always, indeed, an evidence of the purity of the silver, but it is also apt to occasion a loss of silver, though often only a small one.

The formation of the play of colors in the brightening, very probably has its cause in the fact that the constantly renewed, extremely thin coating of oxyd of lead upon the alloy allows the light to pass through it, which is then reflected from the surface of the metal with a certain color. The kind of color is dependent upon the thickness of the coating; and since the latter, on the convex surface of the molten metal, becomes gradually thicker near the edges, different colors are produced in a certain order of succession. This is repeated as long as the oxyd of lead absorbed at the sides is repro-

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duced on the surface, which ceases when the silver becomes pure.

According to *Levol*, the brightening is produced by the oxygen absorbed by the molten silver, which unites with the sub-oxyd of copper taken up by the cupel, and changes it to oxyd, whereby a flash of light is produced (?). With silver not containing copper the oxygen is given out in the cooling, and causes the *sprouting*. That the last appearance is the consequence of a violent escape of absorbed oxygen, the researches of *Lucas* and *Rose* have evidently proved.

The presence of *gold*, according to *Levol*, does not hinder the sprouting, if its quantity is not too large, but the presence of copper and lead does, since the lower oxyds of these metals, going into the cupel, oxydize themselves higher at the expense of the absorbed oxygen.

If the brightening of the globule cannot be seen because of the depth of the cupel, the disappearance of the lead-fumes serves as an indication of its having taken place. By means of a hook the cupel may also be somewhat tipped to one side, and then the state of the process judged of.

The silver globule must appear perfectly brilliant on the upper surface, hemispherical to round or spherical, and silver white; must be easily loosened from the cupel with the globule tongs; and on the bottom, after brushing, must show itself clean, and possess a pure silver-white color, though the latter is here without lustre. Globules which, from cracks or little depressions in the cupel, have roots formed, are to be thrown away as incorrect, since such roots always contain lead. For the weighing of the silver globules it is to be remarked that always, except when lead very poor in silver can be used for the assays, eight centner (or as much as is used in the assay) of assay lead must, at the same time with the assay, be separately scorified and cupelled, and the little silver globule thus obtained is, in the weighing, to be laid in

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the scale with the weights, as the amount contained in the lead used, and thus deducted.

The globule of silver obtained in the silver assay is never chemically pure, but only fire-refined. But the contamination by foreign matters is so trifling that in the assay of ores no further notice is taken of it. These impurities, which may vary according to the character of the constituents of the assay substance, compensate in part, yet not entirely, for the loss by the *absorption of the cupel* (page 104).

The process of cupellation will be still further treated later under silver alloys.

In different mining districts special rules exist as to within what degree of accuracy the amount of silver must be given.

In Saxony the quantity of silver is given with—

.05 —	.25	pounds	in the	centner,	to	within	·005	of a pound.
.25 —	2.00	"	"	"	"	"	.01	"
2.	and more	"	"	"	"	"	.02	"

The assay is made but once, or is several times repeated, according to the quantity of silver in the ore; and the following rule:—

With	.01 —	.4	pounds	silver	in the	centner,	2	times.
"	.4 —	.8	"	"	"	"	3	"
"	.8 —	1.5	"	"	"	"	4	"
"	1.5 —	3.	"	"	"	"	6	"
"	3. —	100.	"	"	"	"	8	"

With the assays that are repeated, each one is weighed to within .005 of a pound, and then the average value calculated.

If the values given by the two assayers differ by .01 of a pound and over, a decisive assay is undertaken by the assay master, which, in case of a remarkable difference, may be again repeated, but the result then found is taken as correct.

At the *Oberharz* works the galena slicks are first assayed for lead (page 21), and the lead-button, if it contains three and three-fourths loth, or less, of silver, immediately cupelled;

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while in the last operation, with antimonial, arsenical, and cupriferous buttons, twenty-five to fifty pounds of assay lead are added. If the quantity of silver amounts to over three and three-fourths loth in the centner, the assay is scorified with eight centner of assay lead. The silver globules are weighed to within one-fourth loth, and the contents given by the three different assayers must agree within one-fourth loth before a decisive assay is reported from them. It is only with the antimonial, arsenical, and cupriferous slicks of *Andreasberg* that with

1—5 loth of silver in the centner,	a difference of	$\frac{1}{2}$	loth,			
$5\frac{1}{4}$—10 "	"	"	"	"	" $\frac{3}{4}$	"
$10\frac{1}{4}$ and over	"	"	"	"	" 1	"

is allowed to pass. Richer ores (the so-called Wascherze or buddle ores) are assayed four times. If an assay, after threefold examination on the part of the three assayers, gives still an unallowable difference, then the assay is again repeated by a master assayer and the three other assayers (general examination assay) in the presence of a commission, and from the results obtained the decisive assay is formed.

B. *Fusion assay for plumbiferous ores poor in silver.*

The examination of plumbiferous silver ores and metallurgical products for silver can, under certain circumstances, be accomplished with perfect safety by first seeking the lead contents of the ore or product by means of a lead assay, and then determining the silver contents by a cupellation of the lead-button obtained. If this is to be accomplished with perfect safety, the silver contents should amount to only a few (not above four) loth, and the lead contents must be thirty per cent. or over, and the assay substance, besides intermingled earthy matters, must contain but little of foreign metals. The more, in such argentiferous and plumbiferous substances, the quantity of blende, of iron pyrites, and of copper, arsenic,

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antimony, nickel, or cobalt compounds increases, the less can this method be used with safety for the determination of the silver; just as little reliable is it, completely isolated cases perhaps excepted, if the percentage of lead falls below that stated, or if the quantity of silver is large. A regulation that holds good in the *Hanoverian Hartz* for the assaying of the ordinary lead slicks, prescribes that the quantity of silver shall be found by the scorification assay, and no longer from the argentiferous lead obtained in the lead assay, when it exceeds three and three-fourths loth in the centner of ore. With particular slicks that are otherwise pure, the silver may amount to somewhat more, before a difference shows itself in the result, between the quantity found by the lead assay and that by the scorification assay, provided that the lead amounts to fifty per cent. and over. With all difficultly fusible slicks, however, and still more with those strongly contaminated by other foreign metallic compounds, even with fifty per cent. of lead, a difference soon shows itself with a larger quantity of silver than three and three-fourths loth, and the scorification assay yields more silver.

If it is desired to determine the silver in an ore or metallurgical product from the quantity of lead found in it, everything must be observed that has been prescribed in the lead assay, for the most accurate exhibition possible of the amount of lead. Experience has indeed shown that in the portion of lead that first separates out in the lead assay, a proportionally greater quantity of silver is found than in that which separates later, so that a partially unsuccessful lead assay sometimes allows the amount of silver in it to be very closely found; but if we wish to be able to *rely* upon an accurate determination of the silver, the separation and determination of the lead must be perfectly successful.

At the *St. Andreasberg silver smelting works*, in the Oberhartz, one centner of slick that contains over four loth of sil-

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ver—instead of being scorified—is charged like an ordinary carbonate of potassa assay (page 21); one and one-fourth centner of assay lead, containing exactly one-fourth loth of silver, is strewed over the carbonate of potassa, the whole covered with chlorid of sodium, and smelted like a lead assay. The button is then cupelled and weighed, and one-fourth loth subtracted from the weight. The same results are obtained by this method as by scorification, but less time is required, and the eating through of the crucible is less to be feared.

If the percentage of silver in an assay substance very rich in lead (which is the case for example with some galenas, litharge, old hearths, etc.), is so small that the globule of silver to be looked for in one centner of the assay substance could no longer be weighed with certainty, then, according to circumstances, more or less lead assays must be made of it. The lead-buttons obtained are either cupelled together on the same cupel, or first scorified together by themselves in the ordinary way, and the button of argentiferous lead obtained then cupelled. The quantity of silver in one centner of the substance is then found by dividing the weight of the silver globule by the number of lead-buttons simultaneously cupelled. Very impure lead-buttons (*e. g.* from dross, skimmings, etc.) must be scorified before cupelling, either by themselves or with four to eight parts of assay lead.

If an ore, etc., to be examined for silver, contains notable quantities of metallic mercury, then in the examination of the same, what is given later upon alloys containing mercury is to be attended to.

c. *Fusion assay for pyritiferous ores and sulphuretted products poor in silver.*

This method of assaying, in which the raw or partially roasted ore is fused in a clay crucible, either with litharge alone or with that and a fusing agent, is based upon the

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affinity of litharge for the earths and oxyds and metallic sulphids. In both cases, especially in the latter, a portion of coal, black flux, or flour is also added. The fusion can be performed either in the muffle or in the crucible furnace; it requires somewhat less time than is frequently necessary for the scorification assay.

1. *A fusion of the assay with litharge alone* is only permissible when a considerable quantity of the latter is used, but then a large quantity of lead is produced for cupellation. By an addition of saltpetre, which oxydizes the sulphids, the quantity of lead can be regulated. An addition of twenty-five assay pounds of borax-glass to one centner of ore is never injurious, and is often necessary for the promotion of a good fusion. From what has been already said (page 113), it appears that in most cases twenty to thirty parts of litharge to one centner of ore are enough; frequently, with a plentiful addition of borax, eight to twelve parts of litharge are fully sufficient.

2. If, by a fusion with litharge alone, too small a quantity of lead is separated, a portion (two to six pounds) of coal dust or flour may be added, or the litharge may be mixed with a few centner of black flux; also litharge, carbonate of potassa, and coal dust or flour, may be used together. Here, likewise, an addition of about twenty-five pounds of borax-glass is to be recommended. By the addition of an alkaline flux a smaller quantity of litharge becomes necessary, and it is usual then not to increase the addition of the latter above eight centner to one centner of ore; with an addition of saltpetre, four parts of litharge suffice. If the assay sample contains lead, an addition of metallic iron is advantageously given. A suitable charging for a plumbiferous matte is, for example, 100 pounds of raw matte, 400 pounds of litharge, 25 pounds of saltpetre, 20 pounds of metallic iron, and a corresponding quantity of fusing and solvent agents.

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The assay having been already intimately mixed with the fluxes, it is always advantageous to cover it over in the crucible with a layer of chlorid of sodium.

To insure the complete collecting of the silver, one centner of the assay substance may also be fused with four to eight centner of litharge and twenty-five pounds of borax, or with four centner of litharge and two to four centner of carbonate of potassa, and after the mass has become fluid, four centner of lead added, either in the form of a round plate or as granulated lead, so long as it is distributed as uniformly as possible over the whole surface.

Instead of adding coal or black flux, to undertake the smelting in coal crucibles, as some assayers have proposed, is less judicious, because then the quantity of lead produced is less under control, and the working of the litharge upon the sulphids is apt to be impaired.

Since in all these assays a puffing up of the fusing mass is caused by the escape of the gases generated, the crucibles chosen must be sufficiently roomy.

Berthier fuses substances rich in nickel and cobalt with ten parts of litharge and two parts of saltpetre at a strong heat, and covers over the molten bath with one to two parts of sheet lead, in order to obtain all the silver in the then resulting button, which cupels well.

The use of the ore, etc., in the roasted state yields, on account of the loss taking place in the roasting, a smaller percentage of silver than raw ore. According to *Malaguti's* and *Durocher's* experiments, blende, for example, lost in roasting three-fourths, galena one fourth to one-third, pyrites one-third of its silver content.

3. In *English* smelting works, according to *Zenner*, rich arsenical and antimonial silver ores, which give unreliable results by scorification, are assayed in the following manner: Two ounces of ore are rubbed fine together with two ounces

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of litharge or minium—the mixture poured into a crucible; one-half to one ounce of carbonate of soda spread over it, and on top are placed about 200 grains of small iron nails, which in the smelting sink down through the mass, are oxydized at the expense of the oxyd of lead, and produce a fluid slag, and also aid in the decomposition of the metallic arsenids and antimonids.

All these methods are intended to supersede the scorification. They aim like the latter at a complete decomposition of the assay substance, an entire collection of the silver in the lead, and a slagging off of the constituents not containing silver. The lead alloy obtained is treated exactly like one obtained by scorification, and worked off on the cupel.

Only in special cases, to be more particularly mentioned further on, with a very small percentage of silver in the assay substance, does a crucible smelting in the manner specified offer advantages over the scorification process. In general the latter is to be preferred, since with it, one is more certain of a good and accurate result than with the crucible smelting. Close and accurate results can certainly be obtained by the latter, only it is to be feared that either a complete decomposition of the assay substance will not be attained, and that the slag will remain argentiferous, or that the silver will be collected in a disproportionately large quantity of lead, and then a loss of silver be sustained through the necessarily longer continuance of the process of cupellation. Besides, the scorification assay offers more convenience, especially when many assays are to be made.

For ores containing sulphid of copper, *Karsten* prefers to the scorification assay a crucible smelting without coal, with twenty parts by weight of litharge and twenty per cent. of borax-glass.

Malaguti and *Durocher* have used for determining the exceedingly small quantities of silver in sulphids a mixture of saltpetre, oxyd of lead very poor in silver, and carbonate of

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soda. The poor oxyd of lead was produced from acetate of lead, and by calcining the latter with bicarbonate of soda a salt was obtained which contained a minimum of silver. In their decomposition, zinc blende reduced seven to nine, pyrites nine to thirteen, copper pyrites and variegated copper eight to ten, arsenical copper glance 6.6, native antimony 2.8, stibnite eight to nine, mispickel six to nine, arsenical compounds of cobalt and nickel five to seven, fahlerz six to ten, pitchblende 0.3, and cadmia from the blast furnace 0.8 parts of lead from litharge. Experimentally, one part of saltpetre reduces four to five parts of lead. A suitable charge for smelting consists of ten grammes of ore, twenty grammes of saltpetre, twenty grammes of litharge, and thirty grammes of carbonate of soda, with a covering of chlorid of sodium.

Pettenkofer obtained by a judicious conducting of the crucible assay, even with richer silver ores, just as much silver as by the scorification assay. With ores containing six loth or less of silver in the centner, he mixes one centner of the assay substance with three parts of calcined acetate of lead and two parts of carbonate of potassa; with more than six loth, one-half a centner of the ore with three centner of acetate of lead, two centner of carbonate of potassa (or instead of the latter, one centner carbonate of soda and one centner carbonate of potassa) and twenty-five pounds of anhydrous sulphate of soda. An addition of carbonate of soda makes the charge more fusible, and a mixture of sulphate of soda proves favorable, since its oxygen consumes the excess of carbon, and the sulphid of sodium formed makes the slag more fluid, and takes up the desilverized sulphids. The assay, covered over with common salt, is heated at first gently for twelve to fifteen minutes in a covered crucible till no further action shows itself in the fluid mass; the temperature is then raised for fifteen to twenty minutes to a low white heat, the crucible taken out, rapped against the floor for the better collection

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of the globules, and after cooling, the lead-button is freed from slag for cupellation.

D. *Fusion assay for earthy substances poor in silver* (*slags, slimes, etc.*).

For this kind of substances the following methods of assaying are in use:—

1st. Two centner of the poor argentiferous substance (*tailings* or *slimes* from the mechanical preparation of the ores, poor slags and similar bodies) are intimately mixed with three to four times their weight of black flux, or with as much of a similarly working mixture of carbonate of potassa, with some (about ten to twelve per cent. of the mixture) powdered charcoal or flour, and put in a clay crucible (Fig. 15 b). The surface of the mixture is then levelled off and strown uniformly over with a quantity of pure granulated lead, equal in weight to the assay sample. The whole is now covered over with a thick layer of decrepitated chlorid of sodium and smelted by a gradually increasing heat in the muffle furnace (one to two hours), or (and then with a cover on the crucible) in the crucible furnace. This heat must be more or less high and continued according to the fusibility of the assay. If the assay is very difficultly fusible, 50 to 100 per cent. of borax are also mixed with it in the charging. The crucibles should not be more than two-thirds full, as the mass rises in the commencement of the smelting. In *Freiberg*, to two centner of slags, etc., three centner of black flux and five to eight centner of assay lead are taken, and a three hours' fire is given in a wind furnace.

According to the capacity of the crucible, one to four assay centner (generally two centner) of the substance can be used for an assay. Eight and more crucibles are uniformly charged in the manner above given with the same assay substance.

After cooling, the crucibles are broken up and the argenti-

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ferous lead-buttons obtained separated from the slag, which, in order that it may retain no silver, must indispensably have been in complete fusion during the smelting. The lead-buttons obtained from 8, 16, etc., centner of the assay substance, are scorified together, without further addition of lead, to a single button, and then cupelled. If the assay lead also contains even a little silver, then at the same time 8, 16, etc., centner of the same must be scorified and cupelled, so as to be able to bring its silver into the account and deduct it. The silver globule obtained by the cupellation now gives the contents of the 8, 16, etc., centner of the assay substance. If, for example, one-fourth loth of silver is found (after deducting that of the assay lead), the substance examined, if sixteen centner were used, contains one-sixty-fourth loth of silver in the centner.

A *modification of this method* is, that instead of the covering with granulated lead, an equal or double the weight of the assay sample of pure litharge is mixed with it in the charging, the rest of the process being as prescribed above. Eight to ten centner of litharge, if this is not perfectly free from silver, must also then be reduced by a lead assay (which see), scorified and cupelled. This modification of the method is to be particularly recommended when the poor argentiferous substance does not contain a large proportion of earthy constituents, but does contain sulphides.

Both these methods are to be especially recommended, because the silver of the assay is collected in a comparatively small quantity of lead, and therefore in the cupellation but little silver proportionally is lost by the absorption of the cupel.

2d. At some silver smelting works it is customary, for determining the amount of silver in *plumbiferous slags, matte that is poor in lead*, etc., to smelt two centner of the substance with carbonate of potassa and a portion of coal dust (or,

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instead of both, black flux), with an addition also of borax, under a covering of chlorid of sodium, in the manner treated of in the lead assay. The lead-buttons obtained from four such assays (thus from eight centner of the assay substance) are then cupelled together on a single cupel. Smelting works (for example those of the *Oberharz*) have chosen this process indeed as the ordinary controlling assay for their daily business, for the reason that it allows at the same time of a more or less accurate determination of the amount of lead. It is nevertheless to be remarked that, where the greatest possible accuracy is required in the determination of the silver, the preceding methods are in general to be preferred.

3d. Another method consists in scorifying the poor argentiferous substance in the usual way with granulated lead (page 107, etc.), ten to thirty times, and then uniting the several lead-buttons obtained in the scorifying, and cupelling them together. If the quantity of lead is too great for one cupel, the several lead-buttons are united and once more scorified together beforehand. The quantity of silver in the assay lead must, even when it is very small, be determined and deducted.

4th. In individual cases, for the most accurate determination possible of a small amount of silver in *a substance not very rich in lead and greatly overcharged with* (*especially sulphur*) *compounds of foreign metals* (*particularly iron, zinc, tin, nickel, cobalt, copper, etc.*), a proceeding partly in the wet way is to be recommended, especially when the copper in the ore is at the same time to be determined in the wet way. This is discussed more minutely under the wet assay of copper (page 75), and consists in decomposing the assay substance with aqua regia. The insoluble residue contains the silver as chlorid of silver, and is completely collected on a filter and dried; the filter, with its contents, is then placed in a scorifier or small clay crucible and covered over with assay lead. This is placed in the muffle with a very gentle heat at first, so that

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the filter may first quietly carbonize. When this is accomplished, the heat is increased so that the lead melts and slags a little. The alloy obtained is then cupelled, and, regard being had to the possible presence of silver in the assay lead, weighed.

5th. For the examination of *poor slags*, the following method may also be sometimes used with advantage:

They are smelted in a clay crucible with fifty to one hundred per cent. of pyrites that is free from gold and silver, a few per cent. of coal dust or colophony, and three parts by weight or less of borax, at a very strong red heat. The slag must in this become completely fluid, so that all the crude matte produced may flow together to a button. This crude matte contains now the collected silver, and the latter is, by a further treatment, *i. e.* by scorification of the matte with assay lead, etc., determined.

II.—ASSAY FOR ARGENTIFEROUS ALLOYS.

Metallic alloys in which lead or bismuth makes up the principal part.

These alloys, if they are pretty rich in silver, are immediately worked off on the cupel (*e. g.*, *Freiberg* and *Oberharz* crude and refined lead) in quantities of four centner. Poorer alloys are, before the cupellation, slagged off in quantities of eight to sixteen assay centner and more on a scorifier, and the buttons concentrated to one. The quantities taken are, for instance, of the Oberharz refined lead with one-eighth loth of silver, eight centner; of the *Freiberg* assay lead, one pound civil weight = fifty grammes = about fourteen assay centner. Such a scorification must also take place if notable quantities of foreign substances (fragments of matte, speiss, copper, antimony, etc.) are mixed with the argentiferous lead, and sometimes lead must be added in the process. Thus, for example, at the *Communion Unterharz* smelting

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works, dross is smelted to lead, and the resulting button scorified with eight centner of assay lead; similarly, the lead-button from litharge, old hearths, and skimmings is scorified with four centner lead.

Argentiferous tin.

This is best treated by first oxydizing it by itself on a scorifier in the muffle. Twenty-five pounds of the oxyd are then mixed with sixteen parts of assay lead and four parts of borax-glass, scorified and cupelled. It may also, in order to facilitate the oxydation of the tin, be melted together with twice its weight of lead, and when the oxydation is finished, assay lead and borax added. The oxydation is greatly promoted if the film which forms is constantly removed to the sides of the vessel with a spatula.

Argentiferous zinc is similarly assayed.

Argentiferous iron, pig iron, and steel.

If the iron, etc., can be had in the shape of filings, it may be mixed with some chlorid of sodium, and oxydized in the muffle on a scorifier. Afterwards, for the scorification, one part of iron is mixed with eight to twelve parts of assay lead, two to three parts of borax, and one part of powdered glass, and proceeded with as usual. If filings or very small pieces cannot be obtained, a weighed quantity is oxydized in porcelain or glass with ordinary nitric acid, the oxyd obtained dried in the vessel itself, and then mixed as above for the scorification. At first a very gentle heat is given in the scorifying, in order to avoid any mechanical loss through the possibility of still escaping vapors. Also, one centner of iron filings, etc., may be heated to redness in the muffle with one-half a centner of sulphur or one centner of pyrites in a small covered crucible, and then scorified in the muffle with twelve to fifteen parts of assay lead, and fifteen per cent. or less of borax.

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It is also to be recommended to heat strongly fifty pounds of the suitably comminuted substance with eight to ten parts of lead in an earthen crucible, then to add sulphur from time to time, and scorify the sulphid of iron formed with lead. With a very hot furnace and not too much iron, the latter may also be scorified with borax and without sulphur, which, however, takes longer.

Metallic alloys which contain mercury (natural amalgam, products of amalgamation, etc.).

These are scorified and cupelled as usual, only, on account of the volatility of the mercury, particular care must be taken that the charged assays be placed in the muffle furnace while it is yet cold, or nearly so, and the latter so slowly heated up that the assays shall only be fused after one to one and a half hours. If the assays are placed in a hot furnace, the volatilization of the mercury, especially if it is present in considerable quantity, takes place so rapidly that it boils, and by this, portions of the assay are sure to be thrown out of the scorifier. With *amalgam*, one centner is weighed out in a watch-glass, then placed upon a previously well heated and dried cupel in the almost cold muffle, and the heat gradually raised for about one and a half hours. After all the mercury is volatilized, the assay is heated to redness and cupelled with six to seven parts of lead. *Metallic mercury*, which contains but little silver, may first be subjected to a cautiously conducted distillation in a glass retort, and then all the portions of glass to which the argentiferous residue adheres treated in the scorifier in the usual way. A somewhat larger quantity of the mercury is then taken for the distillation.

Alloys of silver and copper.

It is an old transmitted custom to call copper, whether pure or combined with several per cent. of foreign bodies (black

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copper), which contains under one loth of silver in the mark, *i. e.* not over ten to twelve marks of silver in the centner, *argentiferous copper.* If the amount of silver rises higher and the copper is pure, it is spoken of as *cupriferous silver*, or *alloyed silver.* The processes for assaying them are somewhat different.

A. ARGENTIFEROUS COPPER.

Under this title are considered *refined copper*, *black copper*, *brass*, *tombac*, *bronze*, *gun metal*, *German silver*, etc. (nickel also would be similarly treated). If the assay sample, besides silver and copper, contains only small quantities of foreign ingredients; if, for example, it is refined copper or good pure black copper, it may be immediately cupelled with sixteen to eighteen parts of lead (compare the following section on alloyed silver). But the more the alloy contains of foreign substances besides copper and silver (gold, lead, and bismuth excepted), the less practicable is it to subject it directly to cupellation. It must then, after a preliminary mechanical comminution which is to be carried as far as possible, be first subjected to a scorification conducted in the usual way. With respect to the quantity of lead with which the scorification is performed, it is a rule never to increase it unnecessarily, and also to promote the slagging by a large addition of borax. For *black copper*, *refined copper*, plumbiferous copper (Darrkupfer and Kiehnstöcke), nine to ten centner of assay lead to half a centner of the assay substance are generally enough. With an increasing quantity of tin and nickel, however, one may be obliged, besides an addition of as high as fifty per cent. of borax, to increase the quantity of lead to twenty times the weight of the assay sample. *German silver* and *alloys containing tin* require, in quantities of fifty pounds, ten to twelve centner of assay lead and twenty per cent. of borax; if very rich in tin, ten centner of

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lead to twenty-five pounds of the substance. The assays are repeated several times according to circumstances, and the lead-buttons concentrated. With substances rich in silver, in order not to obtain too large globules of silver, the mark weight is used instead of the centner weight. The scorification is continued at not too high a heat till only a conveniently small button of lead remains. Any silver that may be present in the assay lead used is determined and weighed.

B. ALLOYED SILVER.

(*Ingot assay, mint assay, fine silver assay.*)

A preliminary scorification does not take place in this assay. The alloy is at once cupelled with a definite quantity of lead. It is generally the custom in Germany to use the mark weight (page 14) for this assay.

For the correct management of this assay it is necessary to determine approximately by the *touch-needle*, by the *color* which the alloy assumes upon heating, or by a *preliminary assay*, the richness of the alloy, unless this has already been ascertained in some other way; for multiplied experience has taught that, for the most accurate possible determination of the silver, the quantity of lead used in the cupellation must bear a certain relation to the composition of the alloy. Too great an addition of lead is followed by a loss of silver, and with too small an addition no pure globule of silver is obtained, as then all the copper cannot pass into the litharge, but covers over in a glutinous state the metallic bath (drowning of the assay).

From the *outer physical appearance* of an alloy consisting of copper and silver, a conclusion may be drawn as to its composition. It is the richer in silver, the greater its specific gravity, the whiter its color, and the more malleable it is, *i. e.* the easier it can be hammered, cut, and filed—also, the

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less ring it has; and conversely, it is the richer in copper, the lighter, the yellower, the harder, and the more sonorous it is. The color on the *touch stone* is taken advantage of in the examination. This test presupposes the preparation of a series of alloys which contain 16, 15, 14, 13, 12, 10, etc., loth of silver in the mark, and which are preserved in the form of little rods (needles) or lenses. Upon a smooth, polished, hard, black stone (basalt, Lydian stone), streaks are now made with the different touch-needles, and by the side of them, streaks with the alloy to be tested. With sufficient practice, the richness can be estimated, by comparing the colors of the streaks, within half a loth (in the mark), or even somewhat closer. If, as in the case of coins and wrought silver-ware, the surface of the alloy has been made richer by dissolving out the copper, it must be scoured or scraped before the streaks are drawn for comparison on the touch stone.

This method, used by gold and silversmiths, may be employed to good advantage, although it has no claim to accuracy; and moreover a small quantity of arsenic, zinc, or nickel, if contained in the alloy, makes it appear richer than it is. The touch-stone is again cleaned off with coal dust and oil, or with pumice-stone powder, by means of a piece of wood covered with leather.

Less accurate is the test by heating very gently in the muffle small pieces of the hammered alloy; whereupon the surface becomes more or less thickly covered with a film of oxyd of copper. Pure silver thus becomes dull, but remains white; fifteen-loth silver becomes uniformly grayish white; fourteen-and-a-half-loth becomes of a dull grayish white, with black streaks on the edges; fourteen- to thirteen-and-three-fourths-loth becomes almost grayish black; and thirteen-and-a-half-loth, and all poorer silver becomes quite black. The temperature in the heating should, however, be neither too

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high nor too long continued, as otherwise the colors do not show themselves properly.

The surest preliminary examination is that in which a small quantity of the alloy, perhaps one-half mark, is cupelled with sixteen times its weight of lead, and then, according to the approximate contents found, the strict assay proceeded with.

For the quantity of lead to be used in cupelling an alloy, according to its richness, tables have been devised, which proceed from the results of direct experience. *Erker* gave the following relations:

If in the mark are contained,		The quantity of lead added must be, in marks,	Ratio of the copper to the lead.
Loth of silver.	Loth of copper.		
15½	½	4	1 : 128
15	1	6	1 : 96
14	2	8	1 : 64
12—13	4— 3	10	1 : 40—53
9—12	7— 4	14	1 : 32—54
4— 8	12— 8	15	1 : 20—30
1— 4	15—12	16	1 : 16—21

D'Arcet afterwards gave somewhat different proportions, as the table on page 142 shows.

From these figures, confirmed in general by experience, it follows that in order to bring the copper into the cupel, more lead must be used in proportion when it is combined with a larger quantity of silver.

The quantity of lead necessary also depends upon the temperature in which it is cupelled. The lower it is kept the more lead is required, and conversely, the higher the temperature the less suffices. Too high a temperature in the cupelling is nevertheless, as has been already stated, always accompanied by a loss of silver. It is a rule never to increase unnecessarily the addition of lead, for which the numbers

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The alloy consists of		Parts of lead required to one part of alloy.	Ratio of lead to copper in the assay.
Silver.	Copper.		
1.000	.000	0.3	— —
.950	.050	3.	60 : 1
.900	.100	7.	70 : 1
.800	.200	10.	50 : 1
.700	.300	12.	40 : 1
.600	.400	14.	35 : 1
.500	.500	16 to 17	32 : 1
.400	.600		26.66 : 1
.300	.700		22.85 : 1
.200	.800		20.00 : 1
.100	.900		17.77 : 1
.010	.990		16.02 : 1
Pure copper	1.000		16.00 : 1

given in the above table are taken as an approximate guide.

Since the absorption by the cupel increases with the temperature, it is preferable to take the amount of lead a little larger than is given in the table, and then cupel at a lower heat.

The size of the cupel to be used varies with the amount of lead added, since experimentally a cupel can absorb its own weight of litharge.

The absolute weight of the unit adopted in the assay is often one-fourth of an assay centner. This weight is taken as one mark, and the lower subdivisions made accordingly. For each assay a mark is then weighed out, or, if the alloy is poor, one-half a mark; but then the two silver globules obtained from the concurring assay and its duplicate are weighed together to within one-fourth of a grain. In *Freiberg* the mark = one gramme is divided into one thousand parts. The weighing is carried to milligrammes, and only the whole milligrammes given, *i. e.* only the whole tenths of

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a per cent. In private sale the weight is given within one-fourth of a grain = about a milligramme. In *France* one gramme or one-half a gramme is taken for each assay. The absolute value of the assay weight is indeed a matter of indifference in itself; the above value, however, has shown itself convenient and suitable for use.

The quantity of the alloy required for an assay, if not at hand in the granulated state, is so far flattened out with a polished hammer on a polished anvil, that it can be conveniently cut up with the shears. The cuttings are allowed to fall into a dish of porcelain, sheet copper, etc., placed underneath. The quantity for the assay and its duplicate is then weighed out upon an accurate globule balance, with the precaution of not taking too small pieces, in order the more certainly to avoid a possible loss. That the weighing must be done with the greatest accuracy, need scarcely be observed. The weighed alloy is wrapped up in as small a square as possible of fine letter paper (*a cornet*) or very thin sheet lead, in which latter case the weight of the lead is to be deducted from that of the proper quantity to be added. Generally only two assays are made at once, but several may be conducted simultaneously, if with nearly equal richness they require an equal quantity of lead.

The quantity of lead required is weighed upon a less accurate balance. No granulated lead is used in these assays, but the quantity requisite for each assay consists of a single piece cut from a thin plate of lead. If many assays of this kind are to be made, it is very convenient to cast the lead in spherical or hemispherical moulds (as musket balls are made), which are so graduated that the pieces cast weigh 2, 3, 8, 10, etc., assay marks. The moulds, in the casting, form at the same time figures upon the lead corresponding to these weights, in order to avoid mistakes. The lead must be entirely, or with the exception of *exceedingly* small traces, free from silver.

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The assays can indeed be conducted in any large muffle furnace of good quality, but generally a smaller furnace is used, partly on account of the saving of coal, partly because a change of temperature can be more readily produced in a smaller furnace.

After the furnace has first been completely filled with coal of a suitable size, the quantity of lead necessary for the assay and its duplicate is placed upon two well-dried and hot cupels, the mouth of the muffle closed with coals, and as soon as the lead is melted and begins to "drive," which with a sufficient heat in the furnace very soon takes place, the alloy is added, and now it also quickly fuses. Some assayers have the custom of first placing the silver on the cupel, and when this is red-hot and the cornet is consumed, of adding the lead. In this way one may, perhaps, get along with somewhat less lead; but also, if the lead is not added soon enough, the silver may fuse, be partially absorbed by the porous cupel, and a portion of it withdrawn from the influence of the lead. (Method at the *Oberharz* and *Freiberg*.) Sometimes a part of the lead is first placed on the cupel, and when this "drives," the alloy wrapped in paper added, and finally, when the paper is burnt, the rest of the lead. (*Mint of Hanover*.) By this method, any metallic globules that remain sticking to the sides of the cupel are washed into the metallic bath, and the temperature is moderated.

The indications already given (page 121) serve for judging of the proper heat in the cupellation. The smoke must circulate briskly, and if much lead is used—for example, with silver amalgam, with twelve-loth silver, etc.—one can at first "drive" with a ring of crystals of oxyd. With refined silver no crystals should appear, as the quantity of lead used is too small, and the brightening would not take place hot enough. It is usual to have the temperature, immediately after the fusing, so high that it has to be somewhat moderated by

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closing the lower draft of the furnace. The temperature of the driving metallic bath can also be lowered, if required, by bringing the cupels, which at first stand in the middle, further towards the mouth of the muffle, or by surrounding the assays with cold cupels or scorifiers, or by holding a cold iron (cooling iron, Fig. 22) over them, or by removing most of the coals from the mouth of the muffle. Poor alloys may at first be kept somewhat hotter than rich ones; almost pure silver needs for a pure brightening, a lower temperature than a poor alloy. The muffle opening remains during the cupellation, excepting the room taken up by one or a few coals, entirely open. The coals serve to keep the cupels from being struck immediately by the draft of cold air. Instead of them small pieces of iron made for the purpose (Fig. 3) may advantageously be used.

As soon as the "driving" has progressed somewhat, a new token is presented by which to judge of it, viz. the color of the portion of the cupel freed from the fluid metal. This must be reddish-brown. If it is white, the assay is too hot; if it becomes black, the assay is too cold.

The temperature is raised by laying a glowing coal in the mouth of the muffle, by opening the draft of the furnace, by pushing back the cupels to the rear of the muffle, and by removing the empty cupels or scorifiers. The success of the assay depends not only on the choice of the right quantity of lead, but also especially upon the proper management of the temperature during the "driving" and the "brightening"; and the latter is only to be learned by careful practice.

The nearer the assay approaches to the brightening, the more spheroidal it becomes.

As soon as the rainbow-play of colors has ceased, a pure brilliant lustre appears; the assay *brightens*, and is now finished. It is gradually and slowly drawn towards the mouth of the muffle, where it is allowed to stand awhile, in

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order not to produce a sprouting by too rapid cooling (page 122). As soon as it is ready to brighten, the mouth of the muffle is half closed in order to exclude the air to some extent, for exactly at this instant the silver absorbs oxygen, and afterwards sprouts. The state of the atmosphere seems also, however, to influence the sprouting. If a large globule of silver is heated long after the brightening, there are formed, along with volatilization of the silver, isolated inequalities or protuberances on the surface of the fluid globule, which sometimes unite into a crust, and after the cooling of the silver globule, possess a dull, silver-white color. According to *Plattner*, such a separation appears to consist of a compound of metallic silver with oxyd of silver, and, analogous to over-refined copper, should be considered as over-refined silver.

With assays that succeed well, the assay and its duplicate will brighten simultaneously or immediately after one another, and the weights of the globules, after cleaning with a brush of hog's bristles, will agree well. If a difference shows itself exceeding the limits prescribed for such, *e. g.* over one-half of a grain in the weight, the assay must be repeated. If the assays of the top and bottom of a bar of silver differ, the difference may be divided into three parts, one-third of it added to the smallest result, and two-thirds subtracted from the highest; for, by experience, the result thus found agrees closely with the real value when the bar is melted.

Besides the difference existing in the weight, it has been remarked that in assays that have been conducted with too much lead, the globules, instead of a strongly marked hemispherical form, have a more spherical one, sprout more easily, and seem to separate of themselves from the cupel, to which, if the assays were not very hot towards the end, they adhere but little. The part which rested on the cupel is then indeed colored yellow by oxyd of lead. If the assays brighten badly; if the silver globule is flat and has sharp edges; if

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gray or black spots of oxyd of copper appear on the surface; and if it adheres very firmly to the cupel—these are indications, if the right temperature was employed, that the proper quantity of lead was not taken for the assay.

After the cessation of the rainbow colors, the brightening should neither come too quickly nor too slowly. If it appears within the needful limits, the globule is lustrous, round (with extremely faint indications of crystalline faces), is easily separated from the cupel, the surface of which is quite dry without sparkling with solidified litharge, and is white and granular below. If the brightening follows too quickly, the globule is as it were polished in some spots, in others dull; it adheres more to the cupel, and is often cellular below. If the brightening proceeds too slowly, the surface of the globule is dull white, shows more or less irregularities, has more or less spots of oxyd of copper, adheres strongly to the cupel, and also indeed contains lead.

The appearance of the cupel sometimes enables us to judge of the constituents of the assay substance. With pure lead the cupel has a straw to an orange-yellow color; copper causes a green or a dark-brown color; iron gives a dark stain, especially shortly after the commencement of the operation, and also occasions a dark ring; zinc leaves behind a yellow stain, and gives out during the process a brilliant flame and copious vapors, which cause not an insignificant loss of silver; tin forms a gray, and antimony a light-yellow slag, which cracks the cupel. The last metals require a large quantity of lead for their proper oxydation.

Since the attention is demanded throughout the whole of the operation, it is usual to carry on only two cupellations at once. The highest that might be allowed is to carry on two different assays, and thus four cupellations simultaneously; but then the muffle must be so broad that four cupels can conveniently be placed in a row side by side.

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In *Freiberg*, one mark of refined silver, with 98.4 to 99.2 per cent. of silver, is charged with four parts of lead; *silver from the amalgamation process*, with 78 to 85½ per cent. of silver, with thirteen to sixteen parts; *silver from the extraction process*, with 98 to 98.6 of silver, with five to six parts of lead. In the *assay of coins* and *old plate*, more lead is taken. Coins, if they have been whitened exteriorly, must first be scoured, and old plate granulated.

In the former *mint at Clausthal*, for the *crucible assay* of the granulated alloy for thalers, containing twelve loth of silver in the mark, forty-two loth of lead were taken to four loth of the assay substance, and in the *stock assay* (of finished thalers) double these quantities; in the assaying of *refined silver* sixteen loth of lead were taken to four loth of the metal. At the *Unterharz*, to sixteen loth of refined silver, forty to fifty loth of lead are taken.

Instead of lead, these alloys can also be cupelled with bismuth. The ordinary bismuth of commerce is, however, generally too impure for this purpose, and must first be purified by cupellation and reduction of the oxyd of bismuth obtained. About half the quantity that would be required of lead suffices for the cupellation, and the globules seldom or never sprout. But as bismuth is more costly, and occasions drawbacks rather than advantage in the operation, its use is not customary. Since bismuth is very fusible, the metal is found in almost constant ebullition, by which small drops are very apt to be thrown out in various directions. Moreover, the bismuth oxyd, which is more fusible than litharge, by its more ready absorption into the pores of the cupel, occasions a larger loss of silver, and the silver globule always retains bismuth. Less porous cupels and a lower temperature may remove these evils to some extent. The brightening is more distinct and decided. No further attention is paid in what follows to the cupellation with the bismuth.

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The *absorption by the cupel*, which takes place in every cupellation, has been already (page 104) mentioned. The amount of this is very variable, and is the greater, the higher the heat in which the cupellation was conducted, the more porous the cupels are, and the greater the quantity of lead used with equal richness of the alloy. Moreover, it varies essentially with the composition of the alloy. This loss is seldom constant, even when the same alloy is cupelled in the same furnace, on similar cupels, and by the same assayer. Hence this method of assaying, though it allows of a higher degree of accuracy than that of any other metal assay in the dry way, has nevertheless an uncertainty in its results. It gives the percentage of silver too small, and that by a *variable* quantity. This loss is estimated by the coin commission at Paris, as the following comparative table on page 150, which is adopted in the assay laboratory of the coin and medallion commission at Paris, gives it.

As already stated, however, these numbers are *not* constant, and vary according to the circumstances under which the work is done.

In *Freiberg* somewhat different results have been obtained. With refined silver the quantity of silver was found .0015 to .002 too small, on account of the absorption by the cupel. In alloys of medium richness the loss given in the table is too low; for example, there was found in the wet way eleven loth 17.6 grains, in the dry way eleven loth 16 grains, whence the difference 1.6 grains = .00555, while by the table it is .00452. But in this assay sixteen parts by weight of lead were used, while the difference in the table followed from eleven parts. According to *Plattner*, fine silver with five parts of lead often gives as high as .009 or 2.592 grains per mark, loss; refined silver with fifteen loth of fine silver in the mark, and five parts of lead gives 1.2 to 1.7 grains = .0042 to .0059 loss.

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True quantity of silver.	Quantity of silver found by cupellation.	Loss, or quantity of silver to be added to that found by cupellation.	True quantity of silver.	Quantity of silver found by cupellation.	Loss, or quantity of silver to be added to that found by cupellation.
1000.	998.97	1.03	500.	495.32	4.68
975.	973.24	1.76	475.	470.50	4.50
950.	947.50	2.50	450.	445.69	4.31
925.	921.75	3.25	425.	420.87	4.13
900.	896.00	4.00	400.	396.05	3.95
875.	870.93	4.07	375.	371.39	3.61
850.	845.85	4.15	350.	346.73	3.27
825.	820.78	4.22	325.	322.06	2.94
800.	795.70	4.30	300.	297.40	2.60
775.	770.59	4.41	275.	272.42	2.58
750.	745.48	4.52	250.	247.44	2.56
725.	720.36	4.64	225.	222.45	2.55
700.	695.25	4.75	200.	197.47	2.53
675.	670.27	4.73	175.	172.88	2.12
650.	645.29	4.71	150.	148.30	1.70
625.	620.30	4.70	125.	123.71	1.29
600.	595.32	4.68	100.	99.12	.88
575.	570.32	4.68	75.	74.34	.66
550.	545.32	4.68	50.	49.56	.44
525.	520.32	4.68	25.	24.78	.22

Earlier investigations (1761 to 1769) by *Tillet*, showed not only that cupellation gives the amount of silver in alloys too small, but also that the cupel contains about double the quantity of silver lacking, and consequently that the assay globule is never quite pure, but always retains some lead and copper. If it is desired to show the presence of these metals, one or several cleanly brushed silver globules are dissolved in pure nitric acid, the solution largely diluted with water, the silver precipitated by hydrochloric acid, the fluid filtered, evaporated till only a small quantity is left, and then tested with caustic ammonia, ferrocyanid of potassium, and sulphuric acid.

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Alloys of silver and gold, and of silver and platinum.

The silver is determined by methods given under the assays of gold and platinum.

SECTION II.

SILVER ASSAYING IN THE WET WAY.

A. *Gay Lussac's volumetric assay.*

The recognized imperfections of the cupellation assay (page 104) induced the French ministry of finance, in 1829, to appoint a special commission to examine the customary modes of assaying and specify changes that might be made in them. *Gay Lussac*, who took part in this commission, proposed a new method already used by him in his laboratory, which proved itself, by further improvement, of such a degree of perfection and practical usefulness that it allows of almost mathematical accuracy, and is now established by law in France, and in the German States that took part in the coin convention of July 30, 1838, for the stamping of coins. *Gay Lussac* describes the process in his work entitled "*Instruction sur l'essai des matières d'argent par la voie humide. Paris*, 1832." In what follows, only a short description of this method of assaying, with the addition of a few remarks, will be given, and for further details the reader must be referred to the work of *Gay Lussac* himself.

According to *Gay Lussac's* method of assaying in the wet way, the true quantity of silver in an alloy is found if a definite weight of the alloy be dissolved in pure nitric acid, and then the quantity of a solution of chlorid of sodium of known strength ascertained, which is exactly sufficient to throw down all the silver from the solution as chlorid of silver.

Thus, then, the percentage of silver is not sought from the weight of the precipitated chlorid of silver, but determined from the accurately found quantity of the salt solution used,

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whose strength is precisely known from previous examination.

Now either the weight or the volume of the salt solution used may be determined. The first requires a somewhat less complex apparatus, but demands more time for its accomplishment than the second method, which has been adopted in practice.

If the assayer wishes actually to obtain the accuracy which can be reached by this method of assaying, it is necessary that he should already know approximately the percentage of silver, either by a cupellation assay, by a preliminary examination in the wet way, or from previous experience. The presence of copper, lead, or any other metal (with the exception of mercury) in the solution of silver has no perceptible influence upon the quantity of chlorid of sodium necessary for its precipitation, so that an equal weight of silver, whether it be pure or combined with other bodies, always requires an equal quantity of solution of chlorid of sodium for its precipitation.

It is known, when all the silver is separated, from the fact that a new and very small addition of salt solution produces no more turbidity in the solution. In order to see any turbidity produced it is necessary that the solution should be clear, and this is obtained by agitating the milky turbidity briskly in the solution for some minutes before each new addition of salt solution, by which means the chlorid of silver collects together and readily and completely settles to the bottom, leaving the solution clear.

For the execution of the wet assay, according to the volume of the salt solution used, it now becomes necessary that a solution of chlorid of sodium should be produced of such strength that each decilitre (= 100 cubic centimetres, or a volume of water that weighs 100 grammes) of the same shall exactly decompose the solution of one gramme of chemically pure silver in nitric acid. This is called the *normal salt solu-*

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tion. Further, a solution exactly ten times weaker than this, the *tenth salt solution*, is to be prepared, each litre of which can precipitate one gramme of chemically pure silver. Moreover, a solution of silver in nitric acid is required, which in one litre of fluid shall contain exactly one gramme of dissolved silver. This is called the *tenth silver solution.*

The apparatus used must consist first of a vessel A (Fig. 28) for the reception and preservation of the normal salt solution. The latter, when the cocks Z′ and R are opened, runs through the tubes Z Z into the glass pipette Q. While this is filling with the solution, the air contained in it escapes from the opened cock R′. The pipette Q is of such a size that, when filled to the mark *a b*, it holds a decilitre of the normal salt solution, and discharges it from its mouth *c*, when this is opened, in a continuous stream. When the cocks R and R′ are closed, the screw V, which is connected with an opening, serves to admit a little air, and thereby to cause a slow out-flowing of the normal solution at *c*. In the metallic cylinder F, a flask of a form similar to Fig. 29 has been placed. It contains the nitric acid solution of the alloy to be examined, and the whole decilitre of the normal salt solution is now allowed to flow from the pipette Q into it. The flask is now again removed from the cylinder F, and when, by previous shaking, its contents have become clear, it is examined with the tenth silver and tenth salt solutions to see whether a turbidity is still produced by either of them. In order to have the silver at once precipitated as completely as possible by the normal salt solution, it is necessary to dissolve for the assay such a quantity of the alloy in nitric acid that the solution may contain as nearly as possible one gramme of pure silver.

Since the contents of the alloy to be examined are already known approximately, or have been determined by a preliminary assay, this preliminary approximate determination is considered as correct, and upon this basis the quantity of the

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alloy calculated, which must be weighed out in order that the nitric acid solution of it may contain one gramme of silver. Previously calculated tables given by *Gay Lussac* save the assayer even this slight calculation.

The tenth silver solution is prepared by dissolving one gramme of chemically pure silver in seven to eight grammes of pure nitric acid, and diluting this solution with distilled water to one litre of fluid. For this purpose a flask, Fig. 30, is used, which, when filled to the mark *a b*, holds one litre of fluid. The tenth silver solution is kept in a flask with a glass stopper. For use in the assay a portion of the fluid is poured into a glass vessel, F, Fig. 31, which holds about half a litre, and is provided with a cork, through which passes a suction pipe P, which is so adjusted that when filled to the mark *c d*, it allows a cubic centimetre (= the volume of one gramme of water) to flow out. In order now to take out by means of the suction tube P one cubic centimetre of the fluid, which corresponds to $\frac{1}{1000}$ of the whole volume in which one gramme of silver is now dissolved, the tube which has been dipped in the flask F is again raised, while the upper end is closed with the dampened finger, and then by a lighter pressure of the finger, which allows some air to enter, the fluid is allowed to flow from the lower opening *o* till its surface reaches the mark *c d*. The tube is now at once completely closed by a strong pressure of the finger, till it has been brought over a flask, into which it is to empty its contents by the removal of the finger. A cubic centimetre taken in this way is called a *thousandth;* it is easy to allow one-half and even one-fourth of a thousandth to flow out.

For the preparation of the normal salt solution it is taken as a preliminary guide that, if salt and water were pure, 542.740 grammes of chlorid of sodium would be required to 100 litres of fluid (an easy stochiometrical calculation leads to this result). It suffices, however, to use commercial

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chlorid of sodium, of which a pretty large quantity of a solution, saturated at the ordinary temperature of the room, is formed, and this solution filtered and kept on hand. The quantity of salt which it contains is learned by evaporating a definite quantity of it to dryness. If now, for example, it has been found that 100 grammes of this solution yield, after evaporation, twenty-four grammes of dry salt, then for 100 litres of normal salt solution are required

$$24 : 100 :: 542.74 : x = 2261.4 \text{ grammes}$$

of the concentrated salt solution. These 2261.4 grammes of the solution are therefore diluted with water to 100 litres of fluid.

This mixture may be made at once in the vessel A (Fig. 28). After stirring well, we rinse out the tubes Z Z and the pipette Q with this solution, and then proceed to the rectification of the normal salt solution. For this purpose a preliminary tenth salt solution is next prepared by mixing one part by volume of the yet unrectified normal salt solution with nine parts by volume of water. This can be done by filling the pipette Q to the line *a b*, and allowing its contents to flow into a perfectly clean litre flask (Fig. 30), which is then filled with water exactly to the mark *a b*, and the contents well mixed.

With just such a tube as is shown in (Fig. 31), which, when filled to the mark *c d*, can also hold and discharge a cubic centimetre of fluid, *thousandths* of the salt solution may be taken.

At the same time, in each of several flasks of the form shown in (Fig. 29), one gramme of chemically pure silver has been dissolved in pure nitric acid. Into the solution in each of two of these test flasks, one decilitre (*i. e.* the contents of the pipette Q (Fig. 28) filled to the mark) of the normal salt solution to be rectified is now allowed to flow. After the shaking and clearing of the fluid, *one* of these is examined by

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the addition of thousandths from the tenth silver solution; the *other* by the addition of thousandths from the preliminary tenth salt solution. Before each new addition of a thousandth, the solution must have been made clear again by agitation.

If a turbidity is still produced by the tenth salt solution, the normal salt solution is yet too weak; if a turbidity is produced by the tenth silver solution, it is too strong.

We will suppose the above normal solution, for example, to have been found five-thousandths too weak, we then have

$$995 : 22\ 61.4 :: 5 : x = 11.36$$

i. e. we have 11.36 grammes of the concentrated salt solution to add to the normal solution in hand and thoroughly mix with it.

If, on the other hand, the fluid was found five-thousandths too strong, we have

$$1.005 : 100 :: 5 : 497.51$$

i. e. we must add to it 497.51 grammes of water.

In both cases the normal solution is brought nearer the standard to which it must correspond. How close it has been brought, must be found out by testing anew in the same way, after the tubes and pipette (Fig. 28) have been first rinsed out with the new fluid. This testing and rectification must continue till a correct normal solution is produced. But as it is very difficult to keep this solution perfectly accurate, it is considered as well adjusted when the test gives a variation of only one-quarter to half a thousandth over or under the required normal strength. Now for the first time can a correct tenth salt solution be prepared.

For use in assays the latter is kept on hand in exactly such a glass F (Fig. 31), with a suction tube, P, as is used for the tenth silver solution. Every cubic centimetre taken from it with the suction tube, corresponds now to exactly $\frac{1}{1000}$ of the quantity of salt necessary for the precipitation of one gramme of silver. A thousandth of the tenth silver solution

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and a thousandth of the tenth salt solution, mixed together, reciprocally decompose each other completely.

That the preparation of a new normal salt solution proceeds more rapidly, if from a previous normal solution an accurate tenth salt solution can be prepared and kept on hand, is easily seen from what has been already said.

The vessel A (Fig. 28) for the preservation of the normal salt solution may be made of glass, or, as is more commonly the case, of sheet copper, which is well coated on the inside with a suitable varnish, or with pitch, to prevent a working of the salt upon the copper. The cover of the vessel is concave, and has an opening that is closed by a screw-stopper fitted tight with leather. Through the screw-stopper there passes a glass tube, *l*, reaching nearly to the bottom. Through this tube air can enter, but no evaporation can take place: *n* is a stopper by which the glass tube is closed when the apparatus is not in use. The tube Z Z proceeding from the vessel contains a spirit thermometer, which shows the temperature existing in the normal solution. The pipette Q is maintained immovable and vertical by a small wooden apparatus fastened to a wall or window-frame. About three to four inches from the end of the discharging tube of the pipette Q; it passes through an inverted funnel, to which a tube, T, is soldered, that is designed to conduct away the nitrous acid vapors which the funnel collects. The tube T may be either conducted through a window into the open air, or connected with a box, D, in which a lamp or a dish of coals stands to promote the draft, and from which all vapors are drawn through the tube *p* into a chimney.

F is a cylinder of tinned iron, in which a flask of the form Fig. 29 is placed. The latter contains the alloy or the fine silver weighed out for the assay, which was dissolved in it in nitric acid. The cylinder F is firmly connected with the wiping apparatus, M, and with it is easily movable in cleats, L L,

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so that the cylinder or the wiper may be brought under the opening, *c*, of the pipette, as may be required. This wiper consists of a sponge covered over with linen cloth, or of an elastic bunch of iron-wire cloth covered with linen.

When the pipette Q is to be filled with the normal salt solution, its mouth *c* is closed with the finger, the respective cocks R and R′ opened, and the solution allowed to flow in until it rises somewhat above the mark *a b*. The cocks R and R′ are then closed, the finger removed, the end, *c*, of the pipette brought in contact with the wiper, and the solution, by a very slow admission of air through the screw V, allowed to run out till its surface is exactly even with the mark *a b;* the screw V is then closed, and opened anew when the cylinder with its flask has been brought under the opening, so that the contents of the pipette slowly flow into the flask. The last drop or drops which remain hanging in the opening of the tube at *c*, and do not flow out with the continuous stream, are not brought into account in any assay or rectification, and are removed by a fresh use of the wiper.

In order to avoid interchanging them, each flask (Fig. 29) and its stopper is provided with a number. To facilitate the shaking of the flasks *Gay Lussac* has contrived an apparatus (Fig. 32) which holds ten flasks, is supported above by the spring R, and is connected below with a spiral spring. The flasks are made fast to it by small keys, and it must also contain an arrangement by which the stoppers of the flasks are pressed firm during the shaking. The latter is not shown in the drawing.

Still another apparatus holds ten flasks, for dissolving the alloys in them, either in the sand or water bath.

As an example for the practice of the wet way volumetrically, let a coin of the German Confederation (a two thaler = a three and a half guilder piece) be the sample to be assayed. We know that such a coin, in 1000 parts, should contain 900

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parts of silver and 100 parts of copper. A difference of three-thousandths, either above or below this standard, is allowed in its composition by the coinage laws, without prejudice to its legality.

To determine the quantity of the alloy that must be weighed out for the assay, the calculation of this weight is now made, not for the standard of 900 thousandths, but for a proportion of 897 thousandths, since experience has taught that it is far safer and simpler at the end of the assay to find a higher value by the addition of thousandths from the tenth salt solution, than to be obliged to add tenth silver solution, and thus to find it lower than has been supposed in the calculation and weighing out of the alloy. Solutions, to which the tenth silver solution has been added, clear themselves with far more difficulty than those to which tenth salt solution must be added. Frequently they do not become clear at all, so that one is obliged to begin a new assay with a somewhat larger quantity of the alloy.

Since we assume in our example that 1000 parts contain 897 parts of pure silver, we must, in order to have 1000 parts of fine silver, weigh out 1114.83 thousandths of the alloy. But, as it is impossible to weigh accurately upon the balance this fraction of a thousandth, 1115 thousandths, *i.e.* 1.115 grammes are weighed out for the assay. The exact richness is now sought, which corresponds to this round sum, and for this we have $1115 : 1000 :: 1000 : x = 896.86$ *i. e.* we are now going upon the supposition that the alloy, in 1000 parts, contains 896.86 parts of silver, and not 897 parts.

The weighed assay is placed in the flask without loss, with six to ten grammes of nitric acid of 32° added, and dissolved in the water-bath. The nitrous acid formed is driven out of the flask with a little bellows ending in a glass tube bent at a right angle. The flask is now placed in the thin metallic cylinder F (Fig. 28), the pipette Q filled in the manner

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described, and its contents allowed to flow into the flask. The contents of the flask are now briskly shaken for two or three minutes in the shaking apparatus, and after the subsiding of the chlorid of silver and the clearing of the fluid, a thousandth of the tenth salt solution is added by means of the suction tube. If a turbidity is produced at the surface of the fluid, the flask is closed and shaken anew, whereupon a second thousandth of the salt solution is added. This operation is repeated, after shaking in each case, until with a further addition no more turbidity follows.

Suppose that, in order to reach this point, we have been obliged to add four thousandths of the salt solution (which correspond to four thousandths of a gramme of pure silver), we now have all the data required to enable us to determine the silver contents of the piece assayed.

First, it is clear that the last added thousandth cannot be taken into account, as it produced no further effect. There yet remain, therefore, for the calculation, three thousandths. But it may be supposed that even the third thousandth was too much, and that, if only the half of it is counted, the truth will be most nearly approximated. We retain therefore, finally, only $2\frac{1}{2}$ thousandths.

In the 1115 parts of the alloy that were weighed out for the assay, we have now found 1002.5 parts of fine silver. We have therefore,

$$1115 : 1002.5 :: 1000 : x = 899.1$$

i. e. the piece subjected to the assay has, in 1000 parts, 899.1 parts of fine silver.

We seek to avoid as much as possible, being obliged to add many (six to ten) thousandths of the salt solution, and prefer, in a case in which this became necessary, to repeat the assay with a somewhat smaller quantity of the alloy, since errors, though they be but small, are always to be feared when too many thousandths must be added.

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But now, if the first thousandth of the salt solution added had produced no further turbidity, the richness of the piece would be exactly, or under, 896.86. To find it more accurately, we decompose the first thousandth of the tenth salt solution by a thousandth of the tenth silver solution, and proceed, after shaking and clearing each time, with the addition of single thousandths of the tenth silver solution until no further change is produced by them. Let us suppose that of the thousandths of tenth silver solution added—after deducting the last ineffective one—three came into account, we then have

$$1115 : 997 :: 1000 : x = 894.16$$

i. e. the contents of the alloy amount to 894.16 parts of fine silver in the 1000 parts. It would be best, however, in this case to repeat the assay, weighing out for it 1120 thousandths (*i. e.* 1.120 grammes) of the alloy.

It has been always taken for granted thus far that the temperature of the normal salt solution remains constantly the same. But this is not the case, and it will sometimes show a somewhat higher, and sometimes a somewhat lower temperature than that for which it was adjusted. The spirit thermometer in the tube Z Z serves for observing the existing temperature of the solution. *Gay Lussac* has given tables of corrections for variations in the temperature. But instead of using these tables it is better to remove these variations, by adjusting the normal solution for the medium temperature of the room, and then, on each day when assaying is to be done, to first make an assay with one gramme of chemically pure silver, in order to always learn exactly the strength of the normal solution for the temperature at which the work is done. Let us suppose, for example, that it was found that for the precipitation of this one gramme of silver, besides the volume of one decilitre of the normal salt solution, one thousandth, borrowed from the tenth salt solution, is required,

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then is this thousandth to be first deducted in all assays made at the same time, before their value is calculated. This daily testing with one gramme of pure silver is moreover to be preferred, because experience has shown that the strength of the normal solution (perhaps by a working upon the walls of the vessel, evaporation and condensation of drops of pure water in the vessel A itself, or from causes yet unknown) fluctuates slightly, and also because by this the disadvantage already specified above—that the normal salt solution cannot be rectified with absolute accuracy—is removed.

For these silver assays according to the volume of the salt solution used, it is *indispensable* that the volumes of the litre flask, the pipette Q, and the suction tube, should have *precisely* the correct ratio *to each other*. That, on the other hand, the litre flask should hold exactly a litre, is really unessential, provided that the other vessels have a size exactly proportionate to it.

To avoid calculations during the assaying, the tables given by *Gay Lussac* can be used, to which the assayer may add tables previously calculated by himself, going more into detail for frequently recurring special cases.

It has already been stated that in practice the assay according to the volume has been found more convenient than that according to the weight of the salt solution, since, leaving out of consideration the time necessary for weighing out the alloy, thirty different assays can easily be finished in a day, provided that the richness is already known approximately.

Where assaying is seldom done, or one has but few assays to make, the method according to the weight of the salt solution may be used. A normal salt solution is to be prepared, of which one hundred weighed grammes precipitate exactly one gramme of dissolved silver. A graduated glass cylinder (Fig. 27), which holds 120 to 150 grammes, is filled with this normal

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salt solution, to the highest mark, and accurately weighed. The graduation on the cylinder is made to grammes, but gives only an approximate guide to determine the quantity to be poured out. In these assays by weight, the quantity of alloy to be weighed out for each assay remains constantly the same, and amounts to one gramme. If two grammes are to be taken, the normal salt solution must be adjusted accordingly. It is also necessary here that the richness of the alloy to be examined should be already known approximately, that the assayer may be able to judge beforehand how much of the normal salt solution is to be taken, in order to obtain complete decomposition. This quantity (estimated by the graduation) is poured from the opening, *o*, of the tube of the cylinder into the flask which contains the alloy dissolved in nitric acid, and the cylinder with the remaining solution again weighed, to ascertain the weight of the normal salt solution used. The quantity of fluid which it is intended to use cannot, generally, be taken from the cylinder with accuracy, since no quantity smaller than one drop can be poured from it. But this is a matter of indifference. It suffices to weigh accurately the amount of solution used, and that this amount be taken as nearly as possible corresponding to the richness of the alloy. The assay is now finished by a tenth salt, or a tenth silver solution, which is added in thousandths by volume, as in the assay according to the volume of the salt solution.

It is already stated that the presence of mercury influences the quantity of salt solution necessary for the precipitation of the silver, and the assay then becomes incorrect. Whether mercury is present or not in these assays, may be known from the fact that the precipitated chlorid of silver, which otherwise, when exposed to the diffused light in the room, readily and sensibly changes its color, no longer becomes blue, when it contains four to five thousandths of mercury. With three thousandths of mercury even, in the chlorid of silver, no per-

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ceptible coloring is visible, but it appears if the quantity is less.

If such small quantities of mercury are suspected, a portion only (about one-fourth) of the silver is thrown down by solution of salt, when all the mercury comes down with it, and makes itself known by the non-occurrence of a change of color in the chlorid of silver.

In all cases, therefore, where mercury is found in the alloy, the result of the wet assay must be rejected, and only a cupellation assay remains practicable for the examination.

Also the presence of sulphur and tin in the assay sample impairs the practicability of the process. By using concentrated sulphuric acid instead of nitric acid as a solvent agent, *Levol* removes all inconvenience.

Other assays.

1. *Schoffka* dissolves a weighed quantity of cupriferous silver in nitric acid, neutralizes and adds a standard solution of cyanid of potassium, until a light reddish-brown copper precipitate is formed which does not disappear by shaking.

2. Poor argentiferous ores which contain considerable quantities of sulphids, are decomposed by hydrochloric acid or aqua regia, filtered, and the dried residue scorified with lead.

3. Roasted amalgamation ores are examined in *Freiberg* for the silver free from chlorine which they contain, by digesting the chlorid of silver repeatedly with concentrated solution of chlorid of sodium, washing the residue with water, and when dry scorifying it with lead.

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ADDITIONAL REMARKS UPON THE SILVER ASSAY.

Methods for avoiding considerable differences in the silver obtained from specifically light assay powders.

At the smelting-works in *Felsöbánya* the scorification assay for auriferous silver ores is conducted by weighing out the assay powder in the scorifier upon an under layer of granulated Villach lead, then covering it with the same, and scorifying in the muffle. *Von Berks* has remarked that by this method very essential differences in auriferous silver are given with assay powders of very low specific gravity, which has its cause in the fact that these powders, rising to the surface in the gradual fusion of the lead covering, continually swim about on the top with a rotary motion, and form at the rim of the scorifier a circle of dross which encloses more or less particles of the raw assay powder, which, in the pouring out of the scorified lead into the moulds, are never collected with it. This evil would be removed if the weighed assay powder were carefully *mixed* with the granulated lead and then a lead covering given. Every granule of lead is thus almost coated over with the dust of the assay powder, and in the smelting draws it in, absorbs it, and, forming a whole with the rest of the lead grains, carries the metallic portion of the assay powder as completely as possible into the scorified lead.

The latter method has been many years in use at the *Harz smelting-houses.*

Loss of silver in relation to the quantity of lead used in the cupellation.

In the metallurgical laboratory at *London*, experiments have been made by *Hambly*, as to what effect it has on the loss of silver occurring in the cupellation, if different quantities of silver are used with the same *proportional* quantity of

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lead, and what loss of silver is produced by increasing the proportion of lead. These experiments resulted as follows:—

Amount used.		Loss of silver in
Lead.	*Silver.*	1000 parts.
250 grains.	25 grains.	10.67
100 "	10 "	10.35
10 "	1 "	12.25

When five grains of silver were cupelled with quantities of lead increasing from 5 to 175 grains, the loss of silver in 1000 parts increased from 5.5 to 18.8 parts.

Gay Lussac's silver assay.

It has not yet been successfully attempted to add essential changes to *Gay Lussac's* process for assaying silver in the wet way, in spite of its multifarious use in very different localities.

Mohr makes the following remarks upon it.

1. While in the volumetric assay a constant quantity of the sample is generally weighed, and its richness determined by unequal quantities of the titrated fluid, in the silver assay varying quantities of the substance are taken, but constant quantities of the titrated fluid used.

An ordinary burette, on account of its width, permits no very close reading, and its graduation lines cannot be so closely accurate as the single mark on the pipette used in the silver assay.

Hence the assay is conducted by dissolving a quantity of the substance which contains about one gramme of silver, adding 100 cubic centimetres of normal salt solution, which precipitate exactly one gramme of silver, and then finishing the precipitation of the silver by the tenth solution. The quantity of silver in the sample must have been previously determined by an approximate test.

2. *Gay Lussac* recommended to test a strong solution of

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chlorid of sodium for its salt once for all by an evaporation experiment, and to calculate the composition of the normal salt solution from the result of this.

According to *Mohr* a completely saturated solution of salt may be used, in which a difference of temperature makes almost no difference at all in the contents. Ten cubic centimetres of such a solution contain 3.184 grammes of salt. If, then, seventeen cubic centimetres of it are diluted with water to one litre, 100 cubic centimetres of this will precipitate exactly one gramme of silver.

3. *Mohr* has, by the use of caoutchouc tubes, and spring cocks, produced a pipette arrangement which is cheaper than that of *Gay Lussac* with silver tubes and cocks. If the point of the pipette is rubbed with tallow or paraffine, the *Gay Lussac* wiper becomes superfluous.

4. The assay silver is dissolved in dilute nitric acid, free from chlorine, of 1.2 spec. grav. Strong acid dissolves the silver more slowly. The glass is set in a warm place or in warm water, and the glass stopper either removed or put on loosely.

5. The inconvenience that, in *Gay Lussac's* assay, between two examinations and observations, a period must elapse for the fluid to become clear, and that with insufficient clearing the production of a turbidity remains doubtful, *Mohr* has sought to avoid by a modification of the process.

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ASSAY OF GOLD.

GENERAL REMARKS.

THE same peculiarities which so distinguish silver that they are made use of for the assay of this metal in the pure dry way, are also possessed by gold, and that in so high a degree, that all which was said upon the assay of silver holds good also for the assay of gold; so that but few modifications are required, and even these are slight, and necessitated only on account of the peculiar occurrence of gold, or on account of slight differences between its properties and those of silver.

Gold generally occurs in nature in the *metallic* state, and usually in combination with other metals, especially silver (one to forty per cent.), more rarely with mercury, copper, iron, palladium, etc. It is but seldom found mineralized, though besides selenium and tellurium, arsenic and antimony appear to act as mineralizers. In pyrites (*auriferous pyrites*) the gold is generally present in the metallic state. Besides native gold, the principal gold ores are: *gold amalgam* 4 ($Au_2 Hg_5$) + Ag Hg with 36.7 gold, 5 silver, and 58.3 mercury; *sylvanite* Ag Te + 2 Au Te, with 26.3 gold and 14.3 silver, or (Ag, Pb) (Te, Sb) + 2 Au $(Te, Sb)_3$ with 25—29.6 gold, and 2.8—14.6 silver.

An auriferous ore, metallurgical product, etc., is treated exactly like a similar argentiferous one. But the result of the assay, conditioned by the character of the assay substance, is never, or only with the rarest exceptions, pure gold, but an alloy of gold with more or less silver. The peculiarity of the

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gold assay therefore consists particularly in a further separation of the gold from the silver. No instance is known where ores, which contain gold, copper, and lead, do not at the same time contain silver. The gold obtained from washings also is not pure, but contains more or less silver. The process of assaying for gold, therefore—provided that the substance to be examined is not already such an alloy—must first be so directed as to separate the gold contained in the assay sample as an argentiferous alloy; and secondly, to obtain the gold isolated from this alloy in the wet way.

The *wet way* of assaying is more rarely used with ores than with alloys.

Section I.

AURIFEROUS SUBSTANCES WHICH ARE NOT ALLOYS.

Mechanical gold assay.

For the determination of the metallic gold contained in washings and very finely pounded ores, *e. g.* in auriferous pyrites in the raw and roasted states, the miner makes use of a mechanical assay, in which he separates the non-auriferous, specifically lighter portions from the gold by washing them away. In the *Hungarian* and *Transylvanian* gold mines and washings, a small hand washing-trough is used for this purpose; in *America*, a varnished wooden plate of about eighteen inches in diameter. When a few assay centner of ore are placed in a depression in the centre of the plate, water added, and the plate rapidly whirled, the light portions are thrown off over the periphery.

The washing-trough is eighteen to thirty-six inches long, and twelve to eighteen wide, and provided on three sides with a rim two and a half inches high. A few assay centner and more of ore are washed away upon it until a weighable quan-

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tity of gold has collected in one corner, when it is dried on a clay dish.

A practised workman may in this way obtain an approximately correct result, but this process can make no pretension to the name of a scientific assay.

According to *Boussingalt*, pyritiferous ores in which the gold is contained only in the finely divided metallic state, can be accurately examined by first completely roasting them and then washing them on the washing-trough till only pure gold remains behind. The light sesquioxyd of iron, produced by the roasting, then greatly assists the manipulation. *Kersten* has employed this method for the examination of auriferous pyrites, but performed the washing in a glass cylinder, and treated further the auriferous residue, after smelting it with borax and lead. According to the experiments of *Tscheff'kin*, however, a roasting of auriferous ores may perhaps be disallowable, since a not inconsiderable quantity of gold is thus dissipated mechanically. According to *Winkler* and *Becquerell*, this loss of gold is nevertheless not so considerable as *Tscheff'kin* supposes it.

The already almost entirely pure auriferous silver separated by mechanical preparation on a large scale, needs only to be smelted together with some borax (in a black-lead crucible) to free it from small quantities of earthy matter yet possibly adhering to it.

Assays in the dry way.

For the general assay management of ores, metallurgical products, etc., all the methods of proceeding in the dry way are used, which are given for the corresponding assay of silver; only if, as is extremely often the case, the assay substance is very poor, far greater quantities must be used for an assay; since, in order to be able to effect with certainty the further quantitative separation of the gold from the silver, at

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least nine assay pounds of auriferous silver must have been obtained from the cupellation. From this it is evident that with a very poor assay sample, 500 to 600 assay centner, or even more, may be required for an assay; and that only with a very rich assay sample do one or a few assay centner suffice. The vessels used then must be suitable for this weight, or the portion to be fused must be divided among a corresponding number of them.

The following methods are used according to the richness of the assay substance:

1. *The scorification assay.* This is to be recommended with a *rich* assay sample or with one of *medium value*, since otherwise the quantity of lead to be cupelled might become too great. Generally, then, one centner of ore is scorified with eight centner of granulated lead and as high as one-half a centner of borax. This is repeated several (eight to twelve) times, and the buttons concentrated if necessary. According to *Aidarow*, no loss of gold takes place in the scorification, but a loss occurs in the cupellation by the absorption of the cupel. The gold, however, only soaks into the cupel when it has been scorified with lead beforehand. If gold is added to lead that is already fused on the cupel, no loss of gold takes place in the cupellation. The scorification assay may also be employed with poor pyritiferous ores, if from a larger quantity (twelve to fifty assay centner) of them, in the roasted or unroasted state, most of the foreign metals are previously extracted by heating with nitric acid free from chlorine.

2. *Crucible smelting with lead or litharge.* For a poorer assay substance, a crucible smelting of the kind described (pages 127 and 132) is generally chosen. If the other constituents of the assay sample are *earthy* matters, lead is to be chosen as a flux; if, on the other hand, *sulphids* are most predominant, *litharge* is chosen, and little or no coal added.

For *unroasted* ores (twenty to thirty assay centner) a suita-

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ble charging is four parts of carbonate of potassa, eight to twelve parts of litharge, or better, sugar of lead, one-fourth glass and borax, and one-sixth coal dust. From nagyagite the tellurium is advantageously extracted beforehand by treatment with sulphuric acid.

With very poor pyritiferous ores, a civil pound is completely *roasted* in the muffle, or in an iron pan laid over the fire, and previously rubbed over with clay or chalk. The roasted mass is mixed with one-half to one-fourth of a pound of potash or soda glass, one-fourth of a pound of black flux, and one pound of assay lead (or litharge), covered with chlorid of sodium and smelted about two hours either in a single crucible or in a number of smaller ones among which the charge has been distributed. The resulting lead is cut in pieces, and the separate pieces scorified till a *single* button is obtained, which is cupelled. With very poor ores as high as three pounds must be used for the assay.

It is essential in these crucible fusions that the mass should become perfectly fluid, which frequently, *e. g.* in the examination of zinc blende, requires some attention; and further, that with unroasted ores all sulphur compounds be decomposed, since alkaline sulphids formed in the smelting and not again decomposed, as well as undecomposed metallic sulphids, retain small quantities of gold. An addition of *saltpetre* is to be recommended, in order to attain with more certainty the latter object; however, saltpetre easily leads to mechanical loss by the foaming up of the assay, and too large an addition prevents the reduction of the litharge; it is, therefore, only to be used with great caution.

3. *Matte Assay.* For poor gold ores which consist of a mixture of earthy and pyritiferous substances, it is also proposed to fuse them together with equal parts of glass and vitrified borax, with a thick covering of salt, and then to treat further the crude matte thus obtained.

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The alloy of gold and silver with lead obtained by any of these methods is cupelled precisely as was taught with silver; only, as gold is less fusible than silver, the cupels, especially towards the brightening, must be kept somewhat hotter in order to obtain the auriferous silver globule pure. The weight of the globule shows the sum of the amounts of gold and silver in the assay sample, and serves at the same time, after, by a further process, the amount of gold in the auriferous silver has been determined, for the determination of the quantity of silver present, as this corresponds simply to the difference.

If only small quantities of substances very poor in gold are at command, frequently only a trace of gold can be found by the methods given. But by the help of the blowpipe method the amount of gold may then be determined with sufficient accuracy in the following way. An auriferous silver globule is produced from twenty to thirty assay centner of ore, etc., by any of the preceding methods, weighed by the ordinary assay weights, and the silver introduced by the litharge or lead deducted. The globule is then weighed by the blowpipe assay weights, the silver in question likewise deducted, the gold separated from the silver after the method to be hereafter described, and the weight of the globule of gold determined with a measuring rule.

In stating the result of an assay, it is not usually the custom in Germany to give directly the amount of gold per centner of an ore, but to give the quantity of auriferous silver in one centner of ore calculated in marks and loth, and then to add the amount of gold in a mark of the auriferous silver, calculated in carats and grän or denär.

Assays in the wet way.

The following assays may be used:

1. *The method with aqua regia.* With substances *rich in*

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gold, *e. g.* rich gold quartz, one or more assay centner is digested upon the sand-bath with three to four times its weight of aqua regia (four parts chlorhydric acid of 1.178 spec. grav. and one part nitric acid of 1.28 spec. grav.), the solution decanted, the residue cleared up with aqua regia and washed with distilled water. If necessary, it is filtered. As the chlorid of silver forming is apt to coat over the gold, and thus protect it from the acid, the mass must frequently be stirred while in process of solution.

From the solution which contains chlorid of gold, the gold is precipitated in the metallic state. But in order that it may not redissolve in the excess of aqua regia generally present, the solution is evaporated before the precipitation, till all the nitric acid is driven off. This is promoted by a gradual addition of concentrated hydrochloric acid while evaporating. The solution is then diluted with water.

As a precipitant for the gold, we may use:

a. Protosulphate of iron $FeO, SO_3 + 7\,HO$, or *protochlorid of iron* $FeCl + 4\,HO$.

The solution of gold as well as the iron salt is heated to about 70° C, and the latter poured into the former. The gold is thus precipitated as a fine brown powder. $AuCl_3 + 6\,FeO, SO_3 = Au + Fe_2Cl_3 + 2\,(Fe_2O_3, 3\,SO_3)$.

When a filtered sample is no longer rendered turbid by protosulphate of iron, the fluid is decanted, and the gold, which has separated in compact clumps, washed thoroughly, ignited, and weighed. Should it not be perfectly pure, it may be cupelled with a portion of lead, or fused with saltpetre and borax in a clay crucible.

According to *Morin*, protosulphate of iron precipitates completely even $\frac{1}{450}$ of gold; according to *Elsner*, less completely; according to *Levol*, traces of chlorid of silver always dissolve in the aqua regia, and are then likewise reduced by the salt of iron. This method is the one most frequently used.

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b. Oxalic acid, HO, $C_2 O_3$ and *oxalates.* The former, according to *Levol*, yields a pure gold; but for its complete precipitation a longer digestion (24 to 48 hours), at a gentle heat, is required. As fluid is apt to spatter out in the disengagement of carbonic acid that takes place, large vessels must be used.

$$Au\ Cl_3 + 3\ HO, C_2 O_3 = Au + 3\ H\ Cl + 6\ CO_2.$$

Upon this affinity of oxalic acid for solution of chlorid of gold, *Hempel* has founded a volumetric method.

c. Terchlorid of Antimony, $Sb\ Cl_3$, mixed with hydrochloric acid, reduces, according to *Levol*, the moderately warmed gold solution in a few hours.

$$3\ Sb\ Cl_3 + 2\ Au\ Cl_3 = 2\ Au + 3\ Sb\ Cl_5.$$

The gold is placed on a filter, thoroughly washed with dilute hydrochloric acid, and fused in an earthen crucible with borax and saltpetre. To 100 of gold, 200 of terchlorid of antimony are used.

d. Terchlorid of Arsenic. $As\ Cl_3$, produced by dissolving arsenious acid in hydrochloric acid; reduces the gold quickly and completely from neutral and slightly alkaline solutions.

$$3\ As\ Cl_3 + 2\ Au\ Cl_3 = 2\ Au + 3\ As\ Cl_5.$$

This process is to be recommended.

2. *Plattner's method with chlorine gas for poor pyrites and sulphuretted metallurgical products.* A civil pound or more of the assay substance is *completely* roasted either in the muffle, or over a suitable fire in an iron pan which has been several times coated over with clay and dried. The roasted substance is dampened with sufficient water to give it a loose woolly consistency, and put either into a tubulated glass cylinder or into an inverted tubulated retort with the stoppered neck below, the bottom of the vessel being first covered with a layer of small pieces of quartz, over which is spread a

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second layer of clear quartz sand. By heating a mixture of one part binoxyd of manganese, four parts hydrochloric acid, and one part sulphuric acid previously diluted with an equal volume of water, chlorine gas is generated. This is conducted through water in a wash-bottle to free it from hydrochloric acid, and then through the tube into the cylinder, or through a cork in the neck into the retort. The evolution of gas must proceed slowly at first, but more rapidly afterwards. After the green chlorine gas is perceived above the ore, it is still allowed to pass for at least an hour through the damp powder, whose gold is thus changed to chlorid.

During the whole operation the glass cylinder is tightly closed by a previously warmed thin plate of caoutchouc, through which a glass tube, fitted air-tight, conducts the excess of chlorine to the bottom of a glass cylinder, in which is placed stiff bibulous paper, spirally rolled together, and dampened with alcohol, to convert the chlorine into chloral and hydrochloric acid.

If the chlorine is not free from hydrochloric acid, not only will metallic oxyds be dissolved, but also any metallic sulphids and arsenids present will be decomposed, with the formation of sulphuretted and arseniuretted hydrogen, which transpose with the chlorine, and re-precipitate the chlorid of gold already formed. The more metallic sulphids and arsenids remain in the roasted ore, the longer must the chlorine-gas be conducted through it.

When the process is finished the apparatus is taken apart, a short, narrow eduction tube introduced through the cork which closes the tubular opening of the cylinder or the neck of the retort, and the chlorid of gold washed out with hot water into a beaker placed underneath. The solution is mixed with hydrochloric acid, and the gold precipitated in the metallic state by protosulphate of iron (page 174). It is then filtered, well washed, dried, and scorified with assay

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lead and borax, or immediately cupelled with lead. The gold may also be precipitated by hydrosulphuric acid gas, and the sulphid of gold scorified. In this process the silver generally remains in the residue in the state of chlorid; only with bad roasting, when many other chlorids form, the leaching of the mass produces a concentrated solution, in which chlorid of silver is not altogether insoluble, and thus a small quantity of silver may be obtained with the gold.

Allain recommends that, before the treatment with chlorine, the soluble portion should be removed from the roasted pyrites with sulphuric acid.

By this method $\frac{1}{10000}$ of gold, even, may be extracted.

Section II.

AURIFEROUS ALLOYS.

Alloys of gold with silver and copper.

A. *Separation of the gold by means of nitric acid* (Quartation).

The docimastic separation of *gold* from *silver* depends upon the fact that if the alloy is treated with nitric acid, this dissolves the silver, but does not attack the gold, which remains behind in the metallic state. If the assay sample—for example, coins, jewelry, gold from washings, or milling processes, auriferous copper, etc.—still contains *copper* or other metals that can be slagged off, these must first be removed by a *cupellation* with *lead*, as only an alloy that is free from the base metals can be advantageously subjected to the treatment with nitric acid. According to older experiments, the separation of the silver from the gold only succeeds when the alloy contains not more than about one-fourth its weight of gold. More recent experiments, as will be noticed later, allow a larger proportion of gold. If the gold is present in too large quantity, the alloy must first be fused with a pro-

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portionate addition of silver, which, in case copper is present, takes place at the same time with the preliminary cupellation. This operation, on account of the above ratio, has been called the *quartation*, and the whole method of separation with nitric acid, *separation by quartation.*

Copper has a greater affinity for gold than for silver, and is less easily slagged off on the cupel by lead from its combination with gold than when it is alloyed with silver only. Hence, in the cupellation of cupriferous gold, a larger addition of lead is necessary—about twice as large a one as is required with an alloy of silver and copper of corresponding composition. It is even impossible, from an alloy consisting only of gold and copper, to obtain the gold perfectly free from copper by cupellation, since the gold, even with the largest addition of lead, retains small, though only extremely small quantities of copper. By the presence of silver in the alloy, the separation of the copper is much facilitated, and such a quantity of silver must therefore be added in the cupellation to an alloy consisting only of gold and copper, that the quantity of silver shall be about three times that of the gold. An alloy consisting only of *gold* and *copper* can, indeed, be examined at once with nitric acid, if the quantity of copper amounts to at least one and a half times that of the gold; but this method is inferior to the usual quartation, for such an alloy increases, by oxydation of the copper or by a certain brittleness, the difficulty of the necessary lamination; then the separation of the last portions of copper is more difficult, requires longer boiling with nitric acid, and the little rolls of gold more easily break up. Alloys of gold and copper only, however, seldom present themselves, and when they do, they may be scorified with sixteen to eighteen parts of granulated lead; generally they contain more or less silver.

Experience has further shown that, if the assayer would not be exposed to a loss of the noble metals, the *quantity of lead*

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to be used in cupelling an alloy should not exceed certain limits; and also that, if the ratio of the silver to the gold becomes greater or less than that stated, certain modifications become thereby necessary in the treatment of the alloy. It is the general custom for separating the oxydizable metals from gold to use double the quantity of lead required for silver of like richness, which is very simply done by taking the gold assay weight half as heavy as the silver assay weight. Since, moreover, as was stated above, in case of a less or greater ratio of the silver to the gold, all the silver is not dissolved by the nitric acid, it is clear that, to manage an assay correctly and accurately, the assayer must already know the general composition of the alloy, so as to be able to determine accordingly the quantity of the *quartation silver*, as well as that of the lead to be used. If, therefore, he has not in some other way (perhaps from the tolerably constant character of an ore—of one and the same species of coin, etc.) a general knowledge of this composition, then in order to obtain it, a preliminary test must be made of the alloy, which only needs to be correct to within about a carat. This consists either of an examination with the touch-stone and prepared touch-needles, or of a true preliminary assay, in which lead and silver are then used in rather a superabundant quantity.

The examination on the *touch-stone* (see page 140) is based upon the fact, that the richer an alloy is in gold the more clearly does a streak drawn with it on a black ground present a pure gold-yellow color, and the less is it attacked by pure nitric acid or by a test acid. This *test acid* consists of ninety-eight parts pure nitric acid of 1.34 spec. grav. (37° Beaumé), two parts pure chlorhydric acid of 1.173 spec. grav. (21° B.), and twenty-five parts distilled water. To judge of the richness of the alloy to be examined, its streak is compared with marks drawn with alloys (*the touch-needles*) whose richness is accurately known. In order to get correctly the streak of the

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alloy to be tested, the surface of the metal must first be somewhat filed away, since this may be impure, or, as with coins and jewelry, it may have been made somewhat richer by boiling with acid, and the so-called coloring of the goldsmith, and a clean fracture is rarely to be obtained. Five series of prepared touch-needles are required. The first series consists of copper and gold, and is called the *red series*, and the proportion of gold increases by half carats in the successive needles. The second series, the *white series*, contains needles of gold and silver, in which the proportion of gold likewise increases by half carats. The third series, a *mixed one*, contains needles in which the quantities of silver and copper are equal, and the proportion of gold also increases by half carats. The fourth consists also of needles for a mixed series, in which the silver is to the copper as 2 : 1, and the gold increases by half carats; and the fifth is also formed of needles for a mixed series, in which the quantity of silver is to that of the copper as 1 : 2. Moreover, in mints and stamping bureaux, alloys are used which correspond precisely to the legal standards. The testing upon the touch-stone begins by determining to which series the alloy to be examined belongs. Then those touch-needles are rubbed against the stone whose marks most nearly approximate in color to that of the alloy. The marks must form a thin continuous layer. A drop of pure nitric acid is now placed upon them with a glass rod, and its comparative effect observed. The acid is allowed to work a short time, and then wiped off, in order to see whether the streak appears unchanged, or whether it has more or less disappeared. The test acid above is also used. This is so composed that it does not work at all upon an alloy containing eighteen carats and more of gold, and with such an alloy the streak, after using the acid, will not be wiped off with a fine linen rag, provided that stone and acid had a temperature of 10 to 12° C. Pure nitric acid produces almost no effect

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upon an alloy of fifteen or sixteen carats fine, and over. The testing on the touch-stone can indeed make no pretension to accuracy, especially where the amount of gold is small, but it yields sufficiently useful results for a preliminary test. It requires, however, a sharp and very practised eye. Moreover, the preparation of the touch-needles is wearisome, as the required proportion is not always quickly reached, nor are good malleable alloys always obtained. The touch-stone, therefore, is in general only used where frequent gold assays are to be made of alloys varying in richness, or where (as frequently with gold plate) an examination on the touch-stone will suffice.

If it is desired to learn the contents closer (*e. g.* within a few grän) than is possible by the touch-stone, half an assay mark of the alloy is cupelled with as large an addition of lead as may be deemed necessary (*i. e.* at most thirty-two parts by weight, or sixteen assay marks), and the pure auriferous silver obtained, weighed. The loss gives the proportion of copper with sufficient approximate accuracy, and thereby the whole amount of gold and silver. This preliminary cupellation is naturally omitted when a pure metallic globule, free from foreign metals, has already been obtained on the cupel by the assay for auriferous silver. If the quantity of auriferous silver produced from a poor assay sample is so small that it does not well allow of a preliminary assay, the touch-stone must be used, or a somewhat different method followed, as will be specified later.

The gold and silver alloy obtained on the cupel, if it has a deep-yellow color, is quartated with three times its weight; if the color is very light-yellow, with twice its weight, and if it is pure white, with an equal weight of silver, *i. e.* a sufficient quantity of lead is placed on the cupel, and when this "drives," the auriferous silver and the quartation silver are simultaneously added. After the cupellation, the metallic

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globule is flattened out and digested with moderately strong nitric acid, till no more red vapors are evolved. It is then heated to boiling, after which, the gold obtained is thoroughly washed, ignited, and weighed.

If the assayer, by one of these preliminary examinations, or otherwise, has a previous knowledge of the constitution of the alloy, he may then institute the strict assay. The management of the latter varies somewhat according as the alloy contains three parts or less of silver to one part of gold, and is *argentiferous*, or *argentiferous and cupriferous gold*, or according as more, and frequently much more, silver is present in proportion to the gold, so that the alloy consists of *auriferous silver*.

1. *Argentiferous, or argentiferous and cupriferous gold.*

The absolute weight of the assay mark generally adopted for the gold assay in Germany, amounts to $\frac{1}{32}$ loth civil weight, and is correspondingly subdivided into carats and grän—more rarely into decimal parts. In *France*, half a gramme is taken for the gold assay. The absolute value of the assay weight is indeed a matter of indifference, but the above value has shown itself suitable for practice. The amount of gold is generally stated within one-fourth grän (or within one-thousandth in the decimal subdivision, as in France). The balance used, however, must indicate one-eighth grän, or half a thousandth very distinctly. The assay is either made in duplicate with whole marks, or two half marks are weighed and assayed separately, and the correctness of the assay controlled by the closely agreeing weights of the gold produced, but the gold obtained from both the half marks is finally weighed together for the statement of the result.

If an upper and a lower cut from a bar present themselves, half a mark of each is taken, in order presently to be

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able, by comparing the two little rolls in the weighing, to know the difference in the richness of the bar.

From the properly taken and prepared (laminated) assay sample, the quantity required, generally two half marks, is very accurately weighed out, the precaution being observed not to take too small pieces, in order to avoid mechanical loss. If from a piece chosen for the assay a portion has been removed with a fine file, it must be brushed before being replaced on the balance.

The weighed alloy is preliminarily wrapped in a small paper cornet. A quantity of silver perfectly free from gold is now weighed out, which amounts at most to three times the weight of the gold to be expected from the alloy. If, for example, the alloy was found by the preliminary assay to be twelve carats fine, thirty-six carats (one and a half assay marks) of silver are weighed out when a whole mark was taken for the assay, or twice eighteen carats (three-fourths of an assay mark) when two half marks were taken. If the preliminary assay gave at the same time a notable quantity of silver, this must be borne in mind, and so much the less silver weighed out now. This quartation silver is poured into the cornet with the gold.

The silver added must yield no trace of gold in an assay in which three marks are used, but may without harm contain some lead or copper.

The quartation ratio of three parts of silver to one part of gold, though sanctioned by the practice of years, is, according to *Chaudet* and *Kandelhardt*, not an unchangeable and naturally necessary one, since, according to them, the end is better promoted by taking only two and a half parts of silver instead of three. With this ratio, less silver remained in the gold than with the old one of 3 : 1. The greater the quantity of silver taken in proportion to the gold, the less free from silver could the remaining

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gold be obtained, unless the silver exceeded eight times the gold.

According to *Pettenkofer*, the separation of the two metals still succeeds well when to one part of gold not more than one and three-fourths parts of silver are present, provided the concentration of the acid is properly attended to, and the boiling is sufficiently prolonged. The more the ratio of the silver to the gold increases, the more silver remains in the gold, and cannot be removed either by concentrated nitric acid or by long boiling. But if this ratio reaches eight, an almost perfect separation takes place.

According to *Rammelsberg*, pure nitric acid dissolves all the silver out of an alloy containing eighty per cent. and more of silver, and leaves all the gold behind; and on the contrary, the separation is imperfect with a proportion of from fifteen to eighty per cent. of silver.

As already stated, twice as much pure lead is generally employed as in the cupellation of silver of equal richness. The lead is best cast in the spherical form.

For the quantity of lead free from gold, that is required in the cupellation, *d'Arcet* has drawn up the following table:

If the gold amounts, in 1000 parts, to	The quantity of lead required is	Ratio of the lead in the assay to the copper, etc.	If the gold amounts, in 1000 parts, to	The quantity of lead required is	Ratio of the lead in the assay to the copper, etc.
1000.	1. parts	———	500.	26. parts	52.600 : 1.
900.	10. "	100.000 : 1.	400.	34. "	56.666 : 1.
800.	16. "	80.000 : 1.	300.	34. "	48.571 : 1.
700.	22. "	73.333 : 1.	200.	34. "	42.500 : 1.
600.	24. "	60.000 : 1.	100.	34. "	37.777 : 1.

Kandelhardt gives the ratios in the table, page 185:

The requisite quantity of lead is chosen according to the results of the preliminary assay, and placed on a thoroughly heated cupel. As soon as it begins to "drive," the cornet con-

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Gold in 1000. parts.	Quantity of lead required.
1000. fine gold	8 times the weight of the alloy.
980. — 920.	12 "
920. — 875.	16 "
875. — 750.	20 "
750. — 600.	24 "
600. — 350.	28 "
350. — 0.	32 "

taining the gold and the quartation silver is added, and the cupellation conducted as was directed (page 144), only with the difference that the heat must be kept somewhat higher throughout the process, but especially at the brightening, in order to obtain a pure globule. By an addition of ten per cent. of copper to a sample that is free from it, a brittleness of the alloy in the subsequent lamination is to be avoided. One-half of the lead is also sometimes placed on the cupel first, when this "drives," the alloy added, and then the rest of the lead (page 144). The alloy and the silver may either be in the same cornet, or in two separate ones. The cupels at first stand in the back part of the muffle; after they have begun to "drive" they are drawn forward to where silver should brighten, and again pushed back in the muffle, when two-thirds of the lead is cupelled off, so that a perfect brightening may ensue. The draft is mostly open, and towards the end of the operation the mouth of the muffle is partially closed with coals. No crystals of litharge should form, and the resulting globule must be perfectly round, with a crystalline surface. With too cold a brightening, the globule is rough, and apt to crack in laminating. This is also the case if palladium, iridium, etc., are present. With too low a temperature, the hollow of the cupel retains a glassy appearance from oxyds not absorbed, which is accompanied by a considerable loss of gold and silver. Unnecessary heat is however also to be avoided here. Although the globules but seldom sprout, the cupels are nevertheless not to be immediately taken out of the

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furnace after the brightening, as too rapid cooling would render the globules less malleable. The latter are removed from the cupels with the globule tongs, brushed clean, and after being previously heated again, are laminated on a round *anvil*, with light blows from a polished *hammer* with a round face of about one and a quarter inches in diameter. The anvil, in order to protect it from rust, must be covered by a case, and be sometimes rubbed with a piece of wood covered with leather. The lamination requires some caution, in order to completely prevent any cracking. After the globule is somewhat flattened by a few blows of the hammer, it is turned up edgewise, and the edge slightly hammered round with light blows perpendicular to the lines *x*, *x* (Fig. 33), so that it may remain smooth and even, and not become jagged. The globule is now placed on a suitable dish—an inverted cupel answers the purpose—returned to the muffle, and heated to low redness, to remove the brittleness produced by hammering. The lamination is further proceeded with only after the globule is again cold, because it is more apt to crack while hot. The rim is then lightly hammered again, and the heating repeated. The globule thus gradually takes the forms *a*, *b*, *c*, *d* (Fig. 33). The lamination is carried on till a leaf is obtained of one-third of a millimetre in thickness, which after another heating can be easily bent with the fingers. In order to judge correctly the thickness to be given to the laminated plate, either a thick piece of steel, in which a slit of the required thickness is made, into which the leaf will slide without difficulty as soon as it has reached the desired thinness, is used as a measure, or the globule is flattened out into a round leaf of a definite diameter (one, one and a half, or more inches). The first mode of measuring is the most accurate, as the quantity of the quartation silver varies in different assays. If one mark of gold and three marks of silver were taken, the alloy is advantageously flattened out somewhat

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larger than a one-sixth thaler piece (a little larger than a dime). Instead of finishing the lamination with the hammer and anvil, it is very advantageous, after flattening at first somewhat on the anvil, to use a small *pair of rollers* till the leaf assumes a more or less oval form—about twenty-three millimetres long, and twelve millimetres wide—and its thickness becomes everywhere uniform. The use of too high a temperature must be avoided in heating the laminæ, as otherwise they are apt to become blebby or completely fuse. When the required thickness is attained, the leaves, after another heating, are rolled together with a pair of pendulum pliers and the dry finger, into the form of a spiral, but not so closely as to prevent a little space being left between the coils. The pliers must be perfectly clean, and should have no sharp edges. In order to remove any adhering greasy matters coming from the fingers, the little rolls are again moderately heated, then placed in a matrass (Fig. 23, *a*), and treated at first with weak, and then repeatedly with strong nitric acid. *Kandelhardt*, who treats as many as twelve rolls simultaneously with nitric acid, numbers them before rolling them up with a hammer and punches made for the purpose.

This lamination of the globules is indispensable, for otherwise the nitric acid would not penetrate to the centre of the metal and dissolve out the silver. If the leaves are made too thin, the rolls retain no coherency, and are torn to pieces by the motion of the boiling acid, which is apt to cause mechanical loss, and is always injurious to the certainty of the result. Unless the assayer is much pressed for time, he treats each assay, or at most an assay and its duplicate in a matrass by itself, since with all precaution a roll is sometimes torn.

There are different modes in use of treating the gold assay with nitric acid, which must be free from chlorine, sulphuric, and sulphurous acid. The roll or rolls are always covered

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and digested several times with pure nitric acid. The matrass is placed on a suitable support (Fig. 8) that prevents direct contact of the matrass with the coal, and heated over an open coal fire. Fig. 7 shows a support described by *Gay Lussac*, from the laboratory of the stamping bureau at *Paris*. The matrass, M, stands on a perforated plate of iron or on a grate, and the acid vapors, before they can reach the chimney, pass through a glass tube, T, of about two centimetres diameter and a metre in length, that terminates at each end in a smaller tube, *t*. The lower end passes without friction into the neck of the matrass. As the space between the two tubes is so narrow that a layer of fluid remains hanging there and stops it up, the vapors are compelled to pass up into the broader tube, where they are condensed, and again flow back into the matrass, and as in this way nothing is lost by evaporation, a smaller quantity of acid suffices. In order to always allow a free exit for the vapors, the lower end of the tube must be cut off obliquely, as is seen in P; the descending drop then collects at the point, and never stops up the tube. Near the neck of the matrass is an opening, H, about five centimetres high, through which air can pass into the chimney behind it. The floor of this opening is covered with a pane of glass inclined towards the chimney, on which the nitric acid drops, when the tubes, withdrawn from the flasks, hang in their frame, N. Under the plate of glass is another of sheet iron with slits at *e*, against which the neck of the matrass is leaned that it may not fall down.

The first boiling is performed with one and a fourth loth of nitric acid of 22° B. (measured in a graduated glass cylinder) and continued till the red vapors cease; then follows a second boiling for about ten minutes with the same quantity of previously heated acid of 32° B. The third boiling is sometimes, though better not, omitted, and one-fourth of a grän subtracted from the amount of gold obtained by the second

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boiling, as according to experience this amount would be removed by the third boiling. A greater concentration of the acid than 32° B. does no harm; if weaker acid is used in the last boiling, a larger quantity of silver is left undissolved.

After all the silver is dissolved by the last boiling with nitric acid, the acid is poured out, and the matrass and roll washed repeatedly with hot distilled water This washing must be repeated (about three times) with fresh hot water, until the last remnant of nitrate of silver is removed from the residual porous gold. The solution is poured carefully out, and the fresh water allowed to run into the matrass, while the latter is turned, in order to thoroughly rinse its neck. Only pure water—that is, water free from any chlorine compound—is to be used, since chlorid of silver, which may otherwise be formed in the pores of the gold, cannot be washed out with water, and will thus necessarily occasion too high a result. The last rinsing-water, after pouring out, should produce no turbidity when mixed with chlorid of sodium. The matrass is finally completely filled with water, a small crucible of porous, hard-burned clay, placed over its mouth, and both crucible and matrass in this situation inverted, which causes the roll of gold to sink slowly down from the matrass into the crucible. The matrass is now carefully raised so far that the crucible slowly fills with water, and then quickly drawn to one side over the edge of the crucible. The water is now carefully, and with avoidance of any loss of gold, poured out of the crucible. The dull gold has a brownish color, and is very easily broken. It is thoroughly dried in the crucible, which is placed on the shelf in front of the muffle of the assay furnace, and then, in the same crucible, which is provided with a numbered cover, so strongly heated (at a bright red heat) in the muffle, that it assumes a perfect gold-yellow color and some lustre. In this heating, the rolls diminish in volume, and become so firm

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that they may be handled with the forceps and weighed without danger of breaking.

The strong heating of the gold is, according to *Varrentrapp*, indispensably necessary, in order that it may contract and lose its great porosity, since otherwise it would condense a notable quantity of gas during the weighing.

Kandelhardt brings the rolls of gold from the matrass into clay vessels, which, on one-half of the flat bottom, are furnished with grooves. Into these the rolls are shaken, under water, without touching them with the nippers, so that they lie separate, and cannot come in contact with each other. When several rolls are to be treated simultaneously, they are thus the least exposed to injury, and to a concreting together in the heating. In the weighing, the rolls obtained from the assay and its duplicate (or in case the operation has been conducted with two half marks, the separate rolls of this assay) are first laid on opposite scales of the balance. In successful assays they will counterbalance each other. If they differ perceptibly, the assay must be begun anew.

The amount of gold is generally given *too high*, which proceeds from the fact that the small portion of silver, which it is difficult to remove from the roll of gold, cannot be so far separated as not to affect the weight. This remnant of silver is dependent on the proportion of silver added; on the purity of the lead used in the cupellation, and of the quartation silver; on the purity and specific gravity of the nitric acid; on the duration and repetition of the boiling with the acid; on the washing and heating of the roll of gold; and on the admixture of platinum, iridium, and rhodium. More rarely is the quantity of gold found *too small.* This may have its cause in too hot a cupellation or a disproportionate addition of lead, in the use of the gold globules cupelled without the addition of silver, and in the employment of

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impure nitric acid, especially such as is contaminated with an admixture of chlorine and nitrous acid.

It has been determined by experiment that all the silver can be dissolved out from the gold by nitric acid, only when the silver is alloyed with the gold in so large a porportion (at least eight parts to one) that the latter, by treating the alloy with nitric acid, is completely resolved into a fine pulverulent powder. If the gold and silver have such a ratio to each other that the gold remains behind in a coherent roll, it cannot by any kind of treatment with nitric acid be obtained absolutely free from silver. Accordingly, it would be better to add so much silver to the gold, that the latter should be left as a fine powder, if the boiling with nitric acid and the thorough washing and collection of the finely divided gold obtained were not accompanied by more inconvenience and difficulty than would be counterbalanced by the advantage of obtaining the gold free from the last traces of silver. Only with auriferous silver, from which, moreover, the gold cannot be obtained in the form of a roll, is it obtained, as will be shown later, as a fine powder free from silver. In the assay of the richer gold alloys it is the universal practice not to increase the quartation silver above three times the quantity of gold, in order to obtain the gold as a coherent roll, unless in a special case it is desired to institute a controlling assay by obtaining the gold dust.

If, in treating the gold alloyed with three parts of silver, strong nitric acid were used at first, the roll would very likely be torn to pieces, without, however, falling into powder, and thus we should have all the disadvantages of a pulverulent gold, without obtaining it entirely free from silver. *Dilute nitric acid* is therefore always used at first. But this dilute acid now is far from being able to remove all the silver, and the boiling of the roll is, therefore, after the nitrate of silver solution has been carefully decanted, repeated once or twice with

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strong nitric acid, whereby the remnant of silver in the gold is so far diminished that, with proper attention, it allows a correct determination of the gold.

The errors which this remnant may cause become less, the smaller and more insignificant the remnant is after the treatment with nitric acid.

In the conviction that this remnant can never be entirely removed, it has been sought in all gold assays to reduce it to a small, but constant quantity, and for this purpose the following course is pursued.

A considerable quantity of both a weaker and a stronger acid is prepared. The first is generally taken at 22° B. (1.166—1.1864 spec. grav.), the second at 32° B. (1.26—1.2962 spec. grav.). An assay mark of pure gold, produced by repeated solution in aqua regia and precipitation by protosulphate of iron, is then quartated with three parts of silver free from gold, and the roll obtained, digested at first with a definite measured volume (about one ounce) of the weaker nitric acid, which about half fills the matrass, until the evolution of nitrous acid has entirely ceased for some time, which takes about a quarter of an hour. The solution of nitrate is then carefully decanted, and the roll again digested with the stronger nitric acid for a definite, and best not too short a time. The quantity of this acid must likewise be measured, and is generally somewhat smaller than that used for the first boiling. With respect to the time employed in this operation, I have seen different assayers in German mints and emporiums vary from one to ten minutes. After the washing and heating, it is found that the gold has slightly increased in weight. This experiment must, for the sake of certainty, be again repeated in precisely the same manner. Moreover, a few alloys whose composition is accurately known must be examined in the same way, or an assay mark of pure gold and copper in several different proportions is weighed out, quar-

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tated, and the gold separated in the same way. Here also a small increase will be found in the weight of the gold. After the amount of silver remaining behind has thus been found, both with fine gold and with a few (perhaps two or three) different alloys (the legal ratio for gold coins, the usual richness of gold from washings, etc., is chosen), this remnant is then considered as constant or proportional for the intermediate values.

If a gold alloy is now to be examined, it is treated, in the process, with *equal quantities* of the prepared acids of the definite strength, for exactly the *same time*, and otherwise in the *same way* (on precisely similar cupels, etc.). The same quality of silver is also used in the assay which was employed with the pure gold. It must also be seen to that the leaves acquire exactly the same thickness in the lamination as in the assay of the pure gold and the special alloys, since this has a sensible influence on the amount of the residue. From the weight of gold found by the assay, the previously found and determined residue of silver is now subtracted to obtain a true statement of the gold.

The amount of silver retained depends in great part on the duration of the boiling with the stronger nitric acid. If this is continued only for one to two minutes, it may amount to about one grän or even something more, and errors are more apt to occur the larger it is. If the boiling is continued for eight to ten minutes it can be reduced to one-fourth to one-eighth of a grän. I have not been able by this method to reduce it below one-eighth of a grän.

Vauquelin prescribes for the first boiling of fifteen to twenty minutes, a nitric acid of 22° B., and for the second boiling a duration of seven to eight minutes, with an acid of 32° B., but takes no further notice of the residue of silver.

Chaudet digests at first with nitric acid of 22° B., which he allows to work only for a short time. He then replaces this

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acid by a stronger one of 32° B., and allows it to boil for ten minutes. He then decants the acid and repeats the digestion for the third time with an acid of 32° B., which he keeps boiling eight to ten minutes. He now takes no further notice of the remnant of silver, and considers the gold obtained as pure.

The presence of much *platinum* as well as of *iridium* and *rhodium*, especially the last two, is the most prejudicial to this process, as they remain undissolved with the gold (see the respective alloys).

According to *Pettenkofer*, almost all gold from quartation contains a few thousandths of *platinum*, which greatly assists to increase the amount of silver retained in the gold. By fusion with bisulphate of potassa or soda in a platinum capsule, or a porcelain crucible, and washing out the mass with water, almost all the silver may be extracted as sulphate of silver. The presence of platinum makes the gold more brittle; but the former can be removed as platinate of potassa by fusing with saltpetre, though in this process quite a perceptible loss of gold takes place. Platinum disposes gold to oxydation. The presence of silver protects platinum from oxydation.

That a loss of gold takes place in the cupellation if this is conducted at too high a temperature, or if the alloy is cupelled without quartation silver (*Chaudet* states it at one to three thousandths in this last case), is an already long known experimental fact. But that this takes place in a noticeable quantity with a proper cupellation and with the addition of the quartation silver, especially if the alloy contains much copper, was first made clear later by *Kandelhardt*, who is at the same time of opinion that the absorption by the cupel is richly compensated by the silver retained in the gold. If the gold alloy to be examined contains little or no copper, the absorption of gold by the cupel appears to be far less, and hence the residue of silver is not so much diminished as with

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a cupriferous gold. The larger mass also contributes to this result, as it does not lose so much in proportion on the cupel, and cannot be so easily freed from silver.

Levol has also observed a loss of gold on the cupel by the ordinary treatment, and I have found by experiment that this loss of gold amounts to one-fiftieth to one-eightieth of the quantity of silver which is at the same time absorbed by the cupel. *Kandelhardt* bases his treatment of the assay upon his assumption as above; and under the supposition that only two and a half parts of silver have been used in the quartation (a proportion which *Chaudet* also does not disapprove of), gives the following directions with respect to the boiling in nitric acid, which have for their object to reduce the residue of silver to a minimum. Two half assay marks are taken for an assay, and the two rolls obtained are covered with one and a quarter loth of pure nitric acid of 1.20 spec. grav. in a glass matrass of such size that the belly is at least half filled with it, and the matrass is placed over a coal fire. If the assayer wishes to boil several rolls at once in the same matrass, he must be sufficiently adroit to bring the fragile rolls of gold out of the matrass without injury when the boiling is finished. To four rolls two loth of nitric acid are then taken, etc. This first affusion is boiled with the rolls till all red vapors have disappeared from the neck of the matrass. Immediately after the rolls have been placed over the fire, an equal quantity of acid of 1.30 spec. grav. is poured into another small matrass with a narrow neck and a lip for pouring, and this likewise placed over the fire to heat gradually, so that when the first boiling is finished, this stronger acid may also be boiling hot. The matrass with the rolls, now freed from red vapors, is next taken from the fire, a cloth, paper, or leather rag being used as a holder, and the boiling solution of nitrate of silver quickly and skilfully poured off. The second matrass with

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the boiling stronger acid is then seized in the same way with the right hand, while the first is transferred to the left, and the strong nitric acid quickly, but adroitly, poured over the rolls of gold, which are then immediately replaced over the fire. The boiling will at once resume its course, and is continued for ten minutes. If the amount of gold to be expected is over twenty carats (or 850 thousandths), a third boiling must be undertaken in the same way, and likewise with strong acid of 1.30 spec. grav. This also is allowed to proceed for at least ten minutes. If the boiling is irregular, an expedient suggested by *Chaudet*, a small piece of coal thrown into the matrass, facilitates the evolution of vapor, and prevents, as does also a turning of the matrass, a violent spirting up of the fluid.

Kandelhardt by no means considers the gold obtained as absolutely free from a small remnant of silver, but believes that its weight with the above process gives the contents correctly, because this remnant of silver is passably compensated by a small, often scarcely weighable loss, which the gold has suffered in the quartating cupellation, or at least is so far compensated that the difference no longer perceptibly influences the result. *Kandelhardt* prefers a quartation with two and a half parts of silver, to one with three parts, for the reason that his method as above still gave him somewhat too high a value with three parts of silver, and he obtained a more correct result with two and a half parts. In his experiments, however, he used cupels consisting of two parts of fine, well leached hard-wood ashes and one part of not too finely pulverized bone-ash, lined on the inside with fine bone-ash, and performed the cupellation in an iron muffle, in which, after the "driving" had commenced, he drew the cupels forward to the place where silver should brighten, and, when two-thirds of the lead was driven off, shoved them again back in the muffle.

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From what is stated (page 194), respecting the loss of gold on the cupel, it follows of course that if in an alloy consisting of gold, silver, and copper, the gold and silver are both to be determined, two assays must be made, one of which is cupelled without the addition of silver, and from it the whole amount of gold and silver determined (the preliminary assay, page 181, may be used for this purpose), and the other, cupelled with quartation silver, and treated with nitric acid. Should the globule obtained from the first assay be quartated with silver, cupelled for the second time, and used for the determination of the gold, the percentage of gold would necessarily be found too low.

It is moreover indispensable (as both *Chaudet* and *Kandelhardt* recommend) to assure one's self, at least occasionally, of the correctness of the assay treatment, by making controlling assays with alloys whose composition is accurately known, or with pure gold, in which it is best to let alloy and gold accompany the substances to be proved, and go through the process with them.

The *laboratory* arranged for gold assaying in the *Paris mint* by *Peligot* and *Levol*, in which two assayers can make fifteen gold assays at once, has the following construction (Figs. 34 to 41):

a, Gas burners attached to the tube A A′ A″, which receives illuminating gas from a gas reservoir, outside of the place. By means of the cock A, the communication of the gasometer with the burners can be cut off. Each of the latter has likewise a cock for regulating the supply of gas (Fig. 37, burner on a larger scale). B B, Notches in which the necks of the glass matrasses rest while the alloy of gold and silver is treated in them with nitric acid. D D, Shelf on which the matrasses are placed after the boiling with nitric acid is finished. Their mouths are situated under the ventilators *d d*, which are movable on hinges, and are placed over

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the openings C C. E, Slate for noting the time of the boiling. F F, Vessels of porcelain, one of which contains nitric acid of 32° B., and the other distilled water. G, Niches in which are placed three porcelain funnels, *b*, which are labelled on the outside, "nitrate of silver," "nitric acid," and "wash-water," and provided with platinum sieves (Fig. 38), into which the silver solutions and the water from the washing of the rolls of gold are poured, and which retain the little pieces of coal, put into the matrasses to prevent irregular boiling. These fluids run through earthen tubes, H H′ H″, into three flasks, placed in the space I, which may be closed with a door. To remove the acid vapors, the openings, K K′ K″, B, and C, discharge into the chimney of the muffle furnace. J, Cupboard for keeping cupels. *m*, Pan for catching the drops falling from the cocks of the vessels F. Fig. 39, Wooden tongs, for seizing the matrasses while decanting the hot fluids. Figs. 40 and 41, Muffle furnace; *a* large, and *b* small muffle, closed by clay plates *c d*; *e*, door for introducing coal, turning on the hinge *f*, and opened or closed at will, from the front or rear of the furnace, by the handle *g g′ g″*. *h*, Shelf for cupels, etc.; *i*, grate of movable bars; *k*, openings for cleaning the grate, closed by thick plates of fire-clay; *l*, plates, which surround the furnace on all sides; *m*, chimney.

II. *Auriferous silver.*

If an alloy contains more than three parts of silver to one of gold, the gold, separated by boiling with nitric acid, no longer retains the form of the roll, but is resolved partially or entirely, according to the proportion of silver, into powder. Pulverulent gold is formed when the gold and silver are present in the ratio of 1 : 4. But in order to attain a complete solution of the silver by a single treating with weak nitric acid and a single boiling with stronger acid, this ratio,

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according to the experiments of *Kandelhardt*, must be at least as 1 : 8. If less silver is present, the gold dust must be boiled a second time in the stronger nitric acid in order to be sure of a complete solution of the silver. If such an alloy contains *copper* at the same time, it must also be cupelled before the treating with nitric acid. With respect to the lead to be used in this, one must be governed by the character of the alloy. The richer it is in gold in proportion to the silver, the more nearly must the quantity of lead chosen correspond with the proportions given on page 184 for the cupellation of gold; the more the quantity of silver predominates over the frequently very small amount of gold, the more closely does the quantity of lead to be used approximate the proportions given on page 141 for the cupellation of silver, and then, in the cupelling, so high a degree of heat should not be used as in the cupellation of alloys very rich in gold. When the auriferous silver is cupelled to remove the copper, a small loss of silver always takes place through the absorption of the cupel, in precisely the same way as was stated in the cupellation assay of silver. The quantity of silver, after deducting the gold found, must therefore be obtained too small by the amount of this absorption. If, therefore, a very accurate determination of the silver is required at the same time, quantities of the separate, pure metals, exactly corresponding to the alloy, must be weighed out, and cupelled under like circumstances, in order to be able to control this cupel absorption; or the alloy may be subjected to a silver determination after the method of *Gay Lussac* (page 151).

If the quantity of auriferous silver, obtained from the examination of a very poor assay substance, is so small that no preliminary assay can be made of it (page 181), and if the quantity of gold to be looked for is greater than one-eighth of the mass, the auriferous silver must be fused and cupelled with no more lead than is absolutely necessary, and with such

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a quantity of silver free from gold, that the assayer may be certain of having eight parts of silver to one part of gold, and then treated just like ordinary argentiferous silver.

The greater does the proportion of silver become, the less necessary is a lamination of the auriferous globule, and it is omitted altogether when the quantity of gold is but small. In the latter case it is well to warm the nitric acid before introducing the very carefully brushed metallic globule. If the proportion of gold in the silver does not exceed a few carats, a single treatment with nitric acid of 1.2 spec. grav. = 25° B., and a subsequent boiling with strong acid of 1.3 spec. grav. = 34° B. suffice; if the proportion of gold is higher, the assay must be boiled a second time with the stronger acid, or else the first boiling with this stronger acid must be somewhat longer (at least ten minutes) continued. With silver that is poor in gold it generally suffices to cupel two half marks with lead, and then, only once, and without lamination, to boil together the two globules obtained with nitric acid of 30° B., until no more red vapors are evolved. *Kandelhardt* uses the solution of nitrate of silver obtained from previous gold assays, which always contains much free nitric acid, since he has found that the gold dust then agglomerates more together, and is not so finely divided, as in pure nitric acid, and can be better collected and washed. The solution of nitrate obtained must be perfectly clear, and not retain any finely divided gold in suspension.

The washing, collecting, and heating of the fine, more or less blackish gold dust is performed precisely as in the methods given above for richer gold alloys, but requires more attention and greater practice, in order to avoid with certainty all mechanical loss of the finely-divided gold. Before the decantation of the nitric acid solution and the wash-water, the gold dust must have settled completely to the bottom. After inverting the matrass in the crucible, the opera-

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tor may assist the complete descent of the gold dust by a light tapping of the matrass; but for the perfect collection and deposition of the gold, he must have patience, and allow the matrass to stand quietly over the crucible for a sufficient length of time. By skilfully inclining the crucible while pouring out the water, the fine gold dust is brought into a small heap. It afterwards bakes together somewhat in the heating, and can be entirely removed from the crucible by a gentle tapping, when it is immediately, or after cupelling with a little lead, placed on the scale of the balance. Its weight gives the proportion of gold correctly and accurately. It is well, however, here also to control the process, from time to time, by a synthetic weighing out of pure metals, which are then treated precisely like the assay.

B. *Separation of gold by means of sulphuric acid.*

Sulphuric acid has long been employed for separating silver from gold, and in the large way this method is used almost exclusively. It does not however seem to be adapted for a scientific assay, and for this purpose nitric acid is almost exclusively in general use. According to *Chaudet*, rather less gold is almost always obtained by using sulphuric acid than when nitric acid is employed, and it is also stated that the gold retains no remnant of silver; this, however, according to *Pettenkofer's* experiments, may not be the case. For the separation by sulphuric acid, the alloy must likewise contain a pretty large proportion of silver to the gold, or else be previously quartated with silver. Some assayers choose three parts of silver to one of gold. *Chaudet* prefers two of silver to one of gold. The boiling must be repeated a second time and continued for ten minutes, and after each boiling, especially after the last, the roll of gold must be washed with concentrated sulphuric acid before water is poured over it, for sulphate of silver is easily soluble in sulphuric acid, but diffi-

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cultly soluble in water. This method becomes impracticable, particularly on account of the high boiling point (326° C.) of sulphuric acid, and the thumping which takes place in the boiling. It must moreover give false results, if in the cupellation even an exceedingly small quantity of lead (and the case would be almost the same with bismuth) has remained in the metallic globule; any small quantities of platinum present would also remain in the gold, which is not the case in the treatment with nitric acid. Also, instead of boiling with sulphuric acid, the assay may be fused with bisulphate of potassa or soda.

c. *Separation of gold by means of aqua regia.*

The examination of an alloy consisting principally of gold, by dissolving it in aqua regia, and precipitating the gold from the solution with protosulphate of iron (page 174), is inferior to the ordinary process, not only on account of the time required, but because it is attended with many other inconveniences.

From a thinly beaten alloy that contains less than about fifteen per cent. of silver, aqua regia dissolves all the gold, and leaves all the silver behind as chlorid. With fifteen to eighty per cent. of silver in the alloy, all the gold is not dissolved by aqua regia, as the alloy becomes covered with a thick layer of chlorid of silver. Such an alloy may be fused in a porcelain crucible with three parts by weight of pure lead, and then treated with nitric acid, which thus dissolves all the silver and lead, and leaves the gold.

Assays for other gold alloys.

1. *Auriferous bismuth* and *lead* are either directly cupelled, or, with a very small percentage of gold, first scorified, and several buttons concentrated to one.

2. *Auriferous tin* is oxydized in the muffle, twenty-five

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pounds of it scorified with sixteen parts of granulated lead and four parts of borax, and cupelled.

3. *Auriferous iron*, *steel*, or *pig-iron*, is oxydized with nitric acid, the resulting fluid evaporated to dryness, and the dry mass well scorified with eight to twelve parts of lead, two to three parts of borax, and one part of glass.

4. *Auriferous mercury* is scorified, sometimes after previous distillation, with a very gradually increasing temperature, and with eight parts of lead.

5. *Gold containing rhodium* is fused with three to four parts of silver, parted as usual with nitric acid, and the well-washed and dried gold fused at a red heat in a platinum capsule with bisulphate of potassa or soda, whereby the rhodium, together with the remnant of silver, is dissolved, with brisk evolution of sulphurous acid, and the formation of a brownish-red to black salt. The fluid mass of salts is poured off from the gold, and the fusion with bisulphate of soda again repeated, whereupon the fluid salt appears but slightly colored. After this is again poured off, the gold is boiled a few times with distilled water, dried, and ignited.

In order to be certain of the complete removal of the rhodium, the gold is again mixed with three parts of silver, and the above process repeated. A trace of rhodium imparts to the bisulphate of soda a yellowish color, and when this happens, the globule of gold suffers a loss of weight compared with the previous weighing.

6. *Gold containing iridium* is dissolved in aqua regia, whereby the iridium remains behind as a black powder. This is well washed, and the gold precipitated from the diluted solution with protosulphate of iron. In *California gold*, iridium is often found.

7. *Gold containing palladium* is alloyed with three parts of silver, and treated like an ordinary gold assay, when the palladium as well as the silver goes into solution. After

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the latter has been removed from the diluted solution by chlorid of sodium, the former may be precipitated by metallic zinc.

8. *Gold containing platinum* is treated of under platinum (See Bodemann's Probierkunst, page 379, etc.).

ADDITIONAL REMARKS UPON THE GOLD ASSAY.

Gold assay with the washing trough.

Experience shows that this assay gives a smaller quantity of gold than is actually obtained by the cleaning in the large way. It affords, notwithstanding, a quick and cheap means of examining a gang or sand for gold, and by continued comparative observations, a coëfficient may be determined, by the use of which, with similar substances and processes, the true mill-yield of gold may be calculated with tolerable certainty from the yield of the washing trough. Thus for the vein ore stamped at Böckstein and Rauris, from the average of twenty years, this coëfficient is determined at 1.15 and 1.39. The difference between the yield of the washing-assay and the actual product depends, moreover, not only upon the character of the ore, but quite as much upon the skill and management of the extractor of the gold. Above all, however, it must be attended to, that by careful averaging of the supply of crushed ore or sand to be assayed, or where contiguous veins are to be tested, by suitable borings or scrapings a material should be produced for the washing-trough as similar as possible to that used in the large way.

According to *Ramdohr* and *Riehn*, at the mint in *San Francisco*, the fire assay was formerly but very rarely used for determining the gold in the gold-bearing quartz of California. It generally sufficed to pulverize a piece of known

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weight in a mortar, to concentrate the powder sufficiently with water in a wooden or iron pan, and then to amalgamate. The pulverization in this case should not be performed all at once, but the mortar must frequently be emptied, its contents separated with a fine sieve, and the coarser part pounded again, since particles resembling gold leaf are easily lost in the washing.

Practitioners perfectly familiar with the subject, judge the amount of gold pretty correctly with the eye, by pulverizing a small quantity and washing it in the horn, so-called. This consists of a piece of an ox-horn cut off near the root, from which a piece in the form of a trough is cut out lengthwise.

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ASSAY OF MERCURY.

GENERAL REMARKS.

BESIDES the products of amalgamation, the following substances chiefly present themselves for docimastic examination: *Native mercury*, sometimes mixed with silver; *amalgam* = $Ag\ Hg_2$ with 34.8 silver and 65.2 mercury, and $Ag\ Hg_3$ with 26.2 silver and 73.8 mercury; *cinnabar* = $Hg\ S$ with 86.2 mercury, and its mixture with carbonaceous and earthy matters as *liver ore;* and *mercurial fahlerze* (page 50).

The mercury may be determined in the dry way, or partially or wholly in the wet way.

All assays for the determination of mercury in the dry way are based upon the fact that the mercury, whether already free, or set free from its compounds in the process, can be distilled, condensed, and collected.

The mercury obtained is, indeed, never chemically pure, but with a properly conducted operation the impurities are so small that they may be neglected in the assay.

By far the greatest part of the mercury which the metallurgist produces, is obtained from ores which contain it as *cinnabar;* but a small portion is found *native*, and it is still more rarely found *alloyed.* Other natural compounds of mercury that could interest the metallurgist are few. They would, in respect to any assay which might be made of them, follow in general the assay method for cinnabar.

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SECTION I.

ASSAYS OF MERCURY IN THE DRY WAY.

Assays for compounds of mercury with sulphur or chlorine.

1. *Richer cinnabar ores.* Since the sulphuretted compounds of mercury are decomposed by fixed alkaline carbonates or caustic alkalies at an incipient red heat, it is most advantageous to intimately mix the ore to be examined (eight to one hundred loth, civil weight) with about half, or an equal weight, or even somewhat more, of carbonate of soda, carbonate of potassa, black flux, etc., and subject it to distillation. The decomposition then follows at a moderate red heat, at which cinnabar does not sublime without decomposition. Sub-chlorid and chlorid, as well as sub-bromid and bromid of mercury, are, however, in this way partially volatilized undecomposed, if the precaution necessary in this case has been neglected, which is to mix the ore with the carbonate of soda, etc., in the most intimate manner possible, by previously rubbing them intimately together with water and drying them again. If, therefore, *horn quicksilver* should be expected in the ore to be examined, regard must be had to this.

Instead of the alkalies, the ore may also be mixed, though it is not as well, with twenty-five to fifty per cent. of iron filings, or from one-half to an equal weight of carbonate of lime or caustic lime. In the latter case ten to fifteen per cent. of coal-dust is added to facilitate the reduction. In both cases a decomposition is effected only at a higher temperature, at a strong red or even an incipient white heat, at which cinnabar itself is apt to volatilize without decomposition. This does not happen if a mixture of caustic soda and caustic lime is used, which does not fuse like the alkalies alone.

Coal alone, indeed decomposes sulphid of mercury, with the

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formation of sulphid of carbon. But this decomposition is impracticable as an assay method, since it first begins at a temperature in which a great part of the cinnabar volatilizes undecomposed.

By the use of iron filings, metallic mercury and sulphid of iron are very simply formed.

When fixed alkalies and alkaline earths are used, sulphuric acid is produced from the oxygen of the former and a part of the sulphur in the cinnabar, and the alkaline or earthy metal set free takes another portion of the sulphur of the cinnabar to itself. Thus if carbonate of potassa, for instance, is used, sulphate of potassa and sulphid of potassium are formed, with evolution of carbonic acid, and if coal enough is present at the same time, the sulphate of potassa is again reduced to sulphid of potassium.

The *distillation* is generally performed in *clay retorts* or tubes, which are previously coated, if necessary, with a glassy flux. If alkaline fluxes are used, and in pretty large quantity, *iron retorts*, covered with clay on the outside, may very advantageously be employed. After the operation their contents may be soaked and dissolved out with water. The iron retorts are indeed attacked to some extent, but afford the advantage that they are perfectly impenetrable by the mercurial vapor. It is advantageous to cast them so that the neck can be unscrewed.

After the introduction of the mixed and charged assay, it is best to cover it over also with a layer of the flux, and carefully clean the neck of the retort or the empty part of the tube from all that may adhere to it. It is preferable to take a pretty large quantity—eight to one hundred loth, civil weight—for the assay, and with very poor mercurial ores, one hundred loth is the quantity chosen.

On account of the foreign gases evolved in the distillation, the *receiver* should not be joined air-tight to the retort or

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tube. On the other hand, to condense the mercurial vapors quickly and completely, the end of the neck of the retort is wrapped around with a very broad strip of paper, or linen cloth, which is to be kept damp, and the tubular prolongation thus formed is allowed to dip into the water with which the receiver must always be partially filled in the assay of mercury. To allow the neck of the retort itself to pass into the water is not feasible, because then, by a decrease of temperature in the retort, the water might rise up into it. Any vessel, such as a beaker, a confectioner's jar, or the like, may serve as a receiver. Also wet linen bags which are tied round the end of the tube or the neck of the retort, and dip into the water, are used as receivers. The water in the receiver must be kept cold. It is also very expedient to use a *Liebig's* cooling tube (Fig. 24).

The distillation may be performed, with a slowly increasing heat, in any suitable furnace which produces the necessary heat, and allows it to be easily regulated. If the distillation is performed in a retort, it must be seen to that not only the bottom and the sides, but also the top becomes sufficiently heated. The heat to be given depends upon the fluxes chosen. At smelting works where many mercury assays are to be made, a small reverberatory furnace has been constructed especially for this purpose, which allows twenty-six assays to be carried on simultaneously. Such a furnace in use at *Idria* is shown in Figs. 4, 5 and 6.

The distillation is finished when no more new drops of mercury form in the receiver.

The separated mercury has for the most part completely collected in the receiver, though isolated drops may still hang in the neck of the retort. These are made to flow out if possible by a light tapping, but still the neck of the retort must be very carefully swept out with a feather, in order to collect every remnant. Should the mercury obtained not

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flow together well at once, it is usually simply boiled up lightly once with water.

The last remnant of adhering water is removed with blotting paper or burned lime, or expelled by evaporation at thirty to fifty degrees C. The mercury is then placed in a light tared glass vessel upon the balance.

Loss of mercury by scattering, or from similar causes, must be very carefully guarded against in the assay. With a lack of proper care small losses of this kind are most generally the occasion of incorrect and false results.

Great errors might result from this, if retorts and tubes were used that allowed the vapor of mercury to pass through them.

The assay is considered successful when the directions given have been observed, and the results of the assay and its duplicate closely agree, and no undecomposed cinnabar has deposited in the tube or in the neck of the retort, which last, however, can only be the case when the ore has been badly mixed with the reducing agents; or, if lime or iron filings were used, when the heat was too rapidly increased.

This method of assaying has at least such a degree of accuracy that it can serve very well for the control of smelting operations, or for determining the value of an ore. Experience has shown that in general it gives the percentage somewhat lower than it really is; but nevertheless the mercury assay is quite as reliable as many other metal assays, *e. g.* the lead or tin assay. The more the percentage of mercury diminishes the more unreliable do the assays become. With one to five per cent. of mercury, even, the quantity found differs materially from the real one. The mercury is indeed weighed to within one-fourth per cent., though the assays are no longer by any means reliable to this degree. The assay by using from one-half to an equal part of black flux is perhaps the most preferable, as by this the complete decomposition of the

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ore, and this indeed at a moderate red heat, can be best assured.

At Idria eight assays are taken from each furnace charge, each, as one assay centner (one-fourth of a pound, civil weight), mixed with two to three spoonfuls of pulverized lime, and the assays placed in eight iron retorts of a galley furnace (page 209). The receivers are then attached, and the space between the two carefully luted, and the assays heated. Since by experience the tubes lying near the fireplace and the chimney give a smaller resultant quantity of mercury than the middle ones, the former are left vacant. As soon as the empty tubes glow with a bright red heat, the process is finished. The receivers are not cooled. The mercury obtained from each assay is weighed, and the average of the eight assays taken. The percentage of mercury found is only an approximate one. To determine the amount of loss in mercury, *Glowacky* has formed mixtures of metallic mercury and sulphur, and subjected them to distillation with lime. The following results were thus obtained:—

No. of the experiment.	From 100 pounds, which contained in pounds of mercury.	There were obtained;	
		Per cent. of the mercury in the most favorable case.	Per cent. of the mercury in the most unfavorable case.
1.	.01 — .1	47.	0.
2.	.1 — .2	59.	41.
3.	.2 — .5	91.	62.
4.	.5 — 6.	93.	86.
5.	6. — 24.	98.	95.
6.	24. — 48.	98.	96.
7.	48. — 86.	97.	95.

Ores with one to four per cent. of mercury, according to this, give the percentage only very inaccurately.

It is presupposed in the above that, as is indeed the fact in

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most cases, the ore to be examined is not mixed with foreign volatile substances which would be evolved simultaneously with the metallic mercury. But if the ore to be assayed contains arsenic, sulphid of arsenic, and the like, the assay process must be modified.

Berthier, who got hold of an ore containing arsenic, realgar, etc., and cinnabar from *Huanca-Vélica*, in *Peru*, found, after manifoldly varied fruitless experiments, the following method best adapted to its examination for mercury:

The ore was heated in a retort with four to five times its weight of litharge. From the litharge, the sulphid of arsenic, etc., a fusible slaggy mass was formed while the cinnabar was decomposed into sulphurous acid and metallic mercury. The mercury volatilized completely at a moderate heat, and collected in the fore part of the neck of the retort and in the receiver. The single precaution which must be observed for the success of the assay consists in only gradually, and only moderately, heating the clay or glass retort, in order to prevent its being perforated by the corroding effect of the litharge before the operation is ended.

2. *Very poor cinnabar ores.* If the assay sample is extremely poor in mercury, the ordinary assay method becomes somewhat inconvenient and uncertain, on account of the large quantity which must then be subjected to distillation in the assay. For this case *Berthier* found it more appropriate to digest the assay sample with aqua regia, wash it thoroughly, evaporate the whole mass of fluid to dryness, and then treat the dry mass, which contains all the mercury as chlorid, further in the dry way. He found that if chlorid of mercury (corrosive sublimate) is heated with litharge, it volatilizes without undergoing any change. If, besides the litharge, coal dust is also added, or if instead of it metallic lead is used in great excess, the chlorid is reduced to subchlorid, which volatilizes, but not the smallest drop of mercury is

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thus produced. The best reducing agent for the chlorid of mercury contained in the dry mass, is black flux, of which three parts by weight are used, and the precaution specified on page 207 observed, to prevent the sublimation of undecomposed chlorid. Since the mass to be subjected to distillation has been greatly diminished by the treatment with aqua regia, and the subsequent evaporation, and no high heat is now required for the decomposition, the distillation may be performed in a glass retort. When the gang in the poor ore is carbonate of lime, all the lime is dissolved out, *before* the treatment with aqua regia, by moderately strong acetic acid.

By this method the smallest trace of mercury in an ore or amalgamation product can be shown and determined by its weight.

Assays for native mercury or amalgam.

Native quicksilver or *amalgam* can be subjected directly to distillation without flux. Since mercury boils and distils over at 360° C., only a little higher temperature than this is here required, but it must be continued long enough to penetrate sufficiently to the interior of the retort.

If artificial amalgams are to be examined as to the quantity of mercury that can be separated from them, they likewise, without further addition, are subjected to distillation. Only a small quantity of them, however—a few loth, civil weight, or even less—is weighed out for the assay. The distillation of these amalgams can be performed in glass retorts, but small iron retorts, whose necks can be unscrewed, are more advantageous.

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Section II.

ASSAYS OF MERCURY IN THE WET WAY.

Volumetric assays.

Volumetric methods have been given for the determination of mercury by *Hempel* and *Liebig*, but they do not admit of general use. *Hempel's* method requires the coöperation of light; *Liebig's* method presupposes the absence of certain metals.

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Fig. 1.

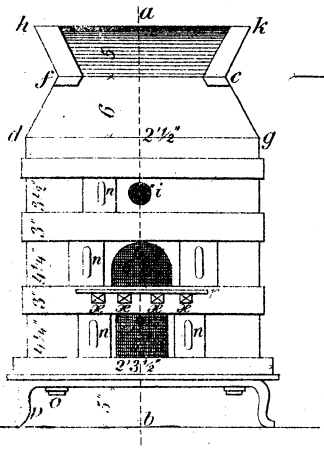


Fig. 2.

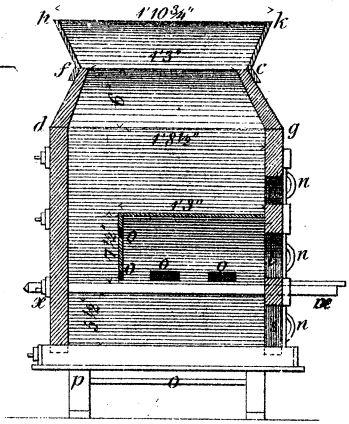


Fig. 3.

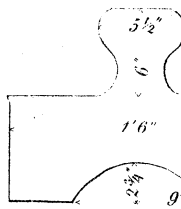


Fig. 5

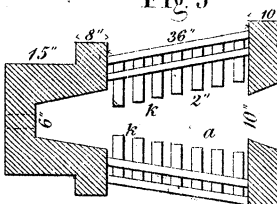


Fig. 4.

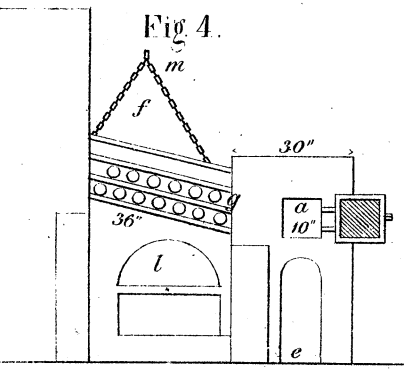


Fig. 6.

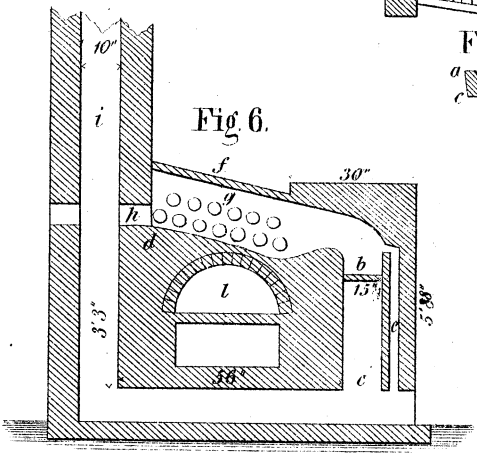


Fig. 9.

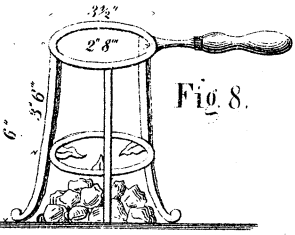


Fig. 8.

Fig. 14.

Fig. 16.

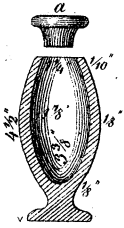


Fig. 19.

Fig. 17.

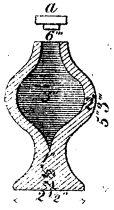
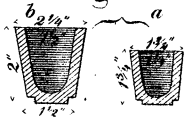


Fig. 18.

Fig. 15.



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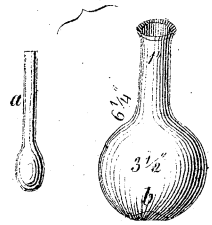

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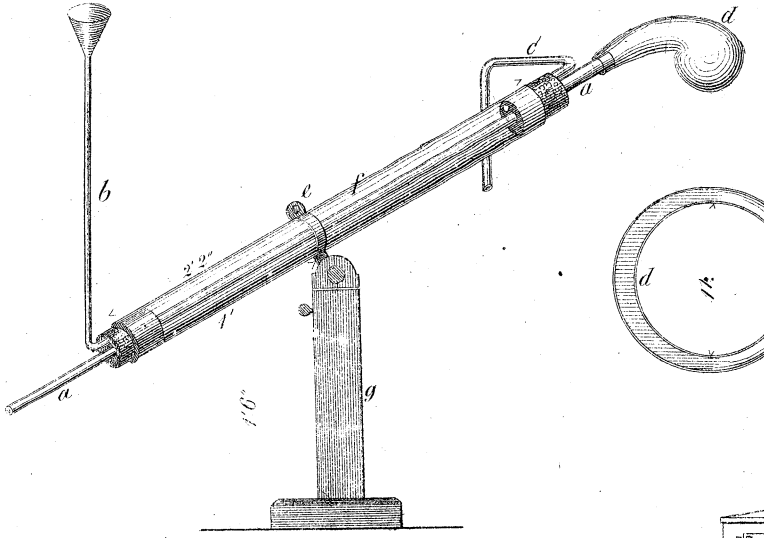
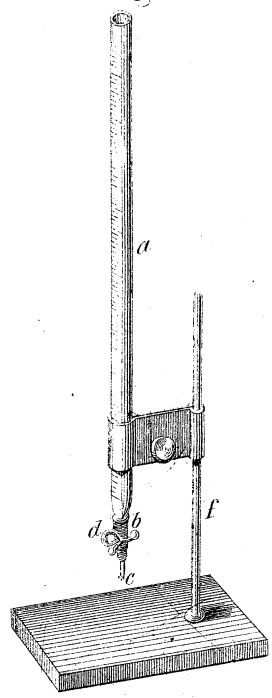


Fig. 29.

Fig. 25.



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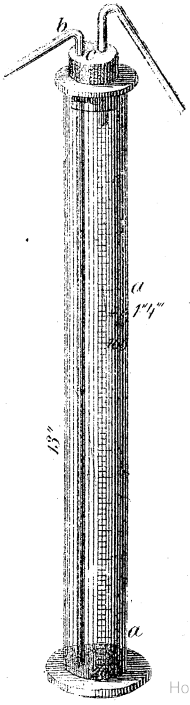

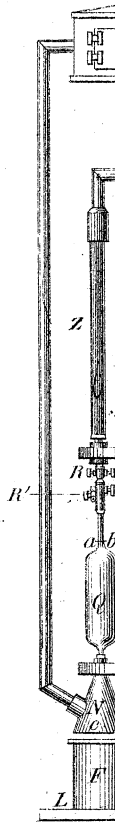

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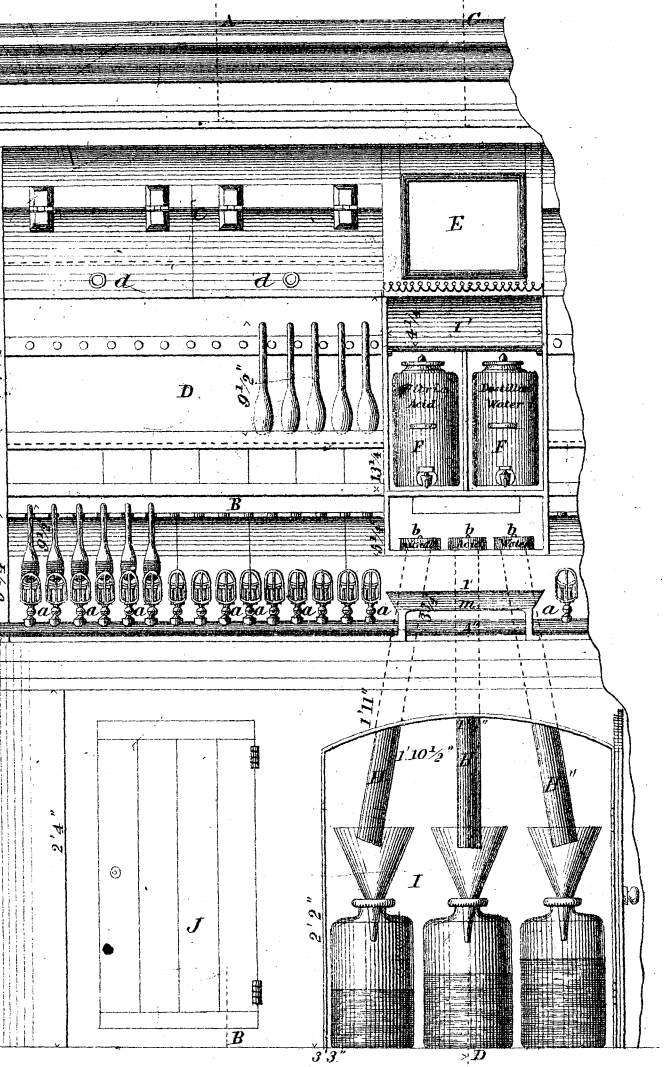
Fig. 34.


A
C
E
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D
9½"
F'
Pure Acid
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Water
Water
Water
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